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CXXIX.—ON THE MOLECULAR REARRANGEMENT OF UNSYMMETRICAL DIACYLPSEUDOTHIOUREAS TO ISOMERIC SYMMETRICAL DERIVATIVES.

BY TREAT B. JOHNSON AND GEORGE S. JAMIESON.

In order to show that the free pseudothioureas, I., are quite stable at ordinary temperatures, Wheeler and Merriam[1] treated

$$H_2NC(SR) : NH.$$
I.

pseudomethylthiourea, in aqueous solution, with an *excess* of alkali and benzoyl chloride. They obtained an excellent yield of benzoylpseudomethylthiourea,[2] II. It has also been shown

$$C_6H_5CONHC(SCH_3) : NH.$$
II.

in papers[3] from this laboratory that those acylpseudothioureas which contain the grouping—CONH—are soluble in alkali.

[1] THIS JOURNAL, **29**, 479 (1903).
[2] J. Am. Chem. Soc., **23**, 293 (1901).
[3] Wheeler and Johnson: THIS JOURNAL, **26**, 410 (1901); *Ibid.*, **27**, 270 (1902).

They dissolve with formation of their sodium salts,[1] which can, provisionally, be represented by either of the two formulæ, III. and IV. :

$$\underset{\text{III.}}{RCONNaC(SR') : NH} \quad \text{or} \quad \underset{\text{IV.}}{RC(ONa) : NC(SR') : NH.}$$

It seemed probable to the writers that a pseudothiourea, I., would react, under proper conditions, with 2 molecular proportions of an acid chloride to give an unsymmetrical diacylpseudothiourea, V. In order to test this assumption we

$$\underset{\text{V.}}{(RCO)_2NC(SR) : NH.}$$

treated pseudomethylthiourea, VI., and pseudoethylthiourea, VII., respectively, in aqueous solution, with the calculated quantity of benzoyl chloride and 2 molecular proportions of potassium hydroxide. They reacted smoothly under these conditions to give the expected unsymmetrical dibenzoylpseudomethylthiourea, VIII., and dibenzoylpseudoethylthiourea, IX., as follows:

$$\underset{\text{VI.}}{H_2NC(SCH_3) : NH} + 2C_6H_5COCl + 2KOH = \underset{\text{VIII.}}{(C_6H_5CO)_2NC(SCH_3) : NH} + 2KCl + 2H_2O.$$

$$\underset{\text{VII.}}{H_2NC(SC_2H_5) : NH} + 2C_6H_5COCl + 2KOH = \underset{\text{IX.}}{(C_6H_5CO)_2NC(SC_2H_5) : NH} + 2KCl + 2H_2O.$$

We now find that these two unsymmetrical derivatives, VIII. and IX., are very unstable. When their alcoholic solutions were boiled, or when the compounds were heated to their melting point they were transformed, smoothly, into the stable, symmetrical dibenzoylpseudomethylthiourea, X., and dibenzoylpseudoethylthiourea, XI. :

[1] We find that, when benzoylpseudomethylthiourea is warmed in benzene with 0.5 molecular proportion of metallic sodium, it reacts with evolution of hydrogen to give a crystalline sodium salt. We intend to investigate it further. T. B. J.

$$\underset{\text{X.}}{C_6H_5CONHC(SCH_3) : NCOC_6H_5.}$$

$$\underset{\text{XI.}}{C_6H_4CONHC(SC_2H_5) : NCOC_6H_5.}$$

This molecular rearrangement is perfectly analogous to the rearrangement of unsymmetrical acylpseudothioureas, XII., to their isomeric symmetrical derivatives, XIII., which was described by Wheeler and Johnson :[1]

$$\underset{\text{XII.}}{RCO(R)NC(SR') : NH} \rightarrow \underset{\text{XIII.}}{RNHC(SR') : NCOR.}$$

$$\underset{\text{XIV.}}{(RCO)_2NC(SR') : NH} \rightarrow \underset{\text{XV.}}{RCONHC(SR') : NCOR.}$$

These isomeric dibenzoylpseudothioureas, XIV. and XV., are sharply distinguished by their properties, and especially by their behavior with alkali and hydrochloric acid. The labile, unsymmetrical derivatives, XIV., show the behavior of triacid amides and are decomposed by alkali and acids with formation of benzoic acid and the corresponding monobenzoylpseudothiourea, XVI., as follows :

$$\left.\begin{matrix} C_6H_5CO \\ C_6H_5CO \end{matrix}\right\rangle NC(SR') : NH + H_2O =$$

$$C_6H_5CO_2H + \underset{\text{XVI.}}{C_6H_5CONHC(SR') : NH.}$$

This behavior with alkali is of especial interest when compared with that of the labile acylpseudothioureas,[2] XII. These were decomposed by alkali with formation of an acid amide and an alkylthiocyanate, according to the following equation :

$$\underset{\text{XII.}}{RCON(R)C(SR') : NH} \rightarrow R'SCN + RCONHR.$$

The instability of the labile diacylpseudothioureas, XIV., towards alkali, explains why Wheeler and Merriam[3] obtained monobenzoylpseudomethylthiourea when they treated pseudo-

[1] THIS JOURNAL, **27**, 270 (1902).
[2] Wheeler and Johnson : *Loc. cit.*
[3] *Loc. cit.*

methylthiourea with benzoyl chloride. They state that an excess of alkali was used. Under these conditions, if any of the dibenzoyl derivative was formed, it would be decomposed into benzoic acid and the monobenzoylpseudothiourea. It is of interest to note here that Stieglitz and McKee[1] prepared benzoylpseudomethylurea, XVIII., by treating pseudomethylurea, XVII., with an *excess* of alkali and benzoyl chloride. It seems probable that, under the conditions employed in our experiments, diacyl derivatives will also be obtained in this oxygen series :

$$\underset{\text{XVII.}}{NH_2C(OCH_3) : NH} \rightarrow \underset{\text{XVIII.}}{C_6H_5CONHC(OCH_3) : NH.}$$

The stable symmetrical dibenzoylpseudothioureas, X. and XI., are soluble in alkali and on adding acid unaltered material is precipitated. On the other hand, when boiled with hydrochloric acid they are decomposed with formation of mercaptan and dibenzoylurea as follows :

$$C_6H_5CONHC(SCH_3) : NCOC_6H_5 + H_2O = CH_3SH + C_6H_5CONHCONHCOC_6H_5.$$

This behavior with hydrochloric acid is widely different from that of the analogous acylpseudothioureas.[2] When these are warmed with hydrochloric acid they are decomposed according to the equation :

$$\underset{\text{XIX.}}{C_6H_5CONHC(SCH_2C_6H_5) : NC_6H_5} + H_2O = C_6H_5CONHCOSCH_2C_6H_5 + C_6H_5NH_2.$$

The action of hydrochloric acid on symmetrical diacylpseudothioureas, XV., is perfectly analogous to that of hydrochloric acid on unsymmetrical, XX., and symmetrical, XXI., acylpseudoureas which has been studied by Stieglitz and McKee[3] and by Wheeler and Johnson.[4] They are converted into acylureas with evolution of ethyl chloride as follows :

[1] This Journal, **26**, 250 (1901).
[2] Wheeler and Johnson : *Loc. cit.*
[3] *Loc. cit.*
[4] This Journal, **24**, 189 (1900) ; **27**, 219 (1902).

$$\underset{\text{XX.}}{RCO(R)NC(OC_2H_5) : NH} \xrightarrow{HCl} RCO(R)NCONH_2 + C_2H_5Cl.$$

$$\underset{\text{XXI.}}{RCONHC(OC_2H_5) : NR} \xrightarrow{HCl} RCONHCONHR + C_2H_5Cl.$$

In the course of our work we investigated the action of parabrombenzoyl chloride and anisyl chloride on pseudomethylthiourea. In these two cases we obtained products which were undoubtedly mixtures of the unsymmetrical and symmetrical diacyl derivatives. When the products were purified by crystallization from alcohol we obtained the stable diparabrombenzoylpseudomethylthiourea, XXII., and dianisylpseudomethylthiourea, XXIII. Their structure was estab-

$$\underset{\text{XXII.}}{BrC_6H_4CONHC(SCH_3) : NCOC_6H_4Br.}$$

$$\underset{\text{XXIII.}}{CH_3OC_6H_4CONHC(SCH_3) : NCOC_6H_4OCH_3.}$$

lished by the fact that they were converted into the corresponding diacylureas, XXIV. and XXV., with evolution of methylmercaptan, when boiled with acids:

$$\underset{\text{XXIV.}}{BrC_6H_4CONHCONHCOC_6H_4Br.}$$

$$\underset{\text{XXV.}}{CH_3OC_6H_4CONHCONHCOC_6H_4OCH_3.}$$

EXPERIMENTAL PART.

Unsymmetrical Dibenzoylpseudomethylthiourea, $(C_6H_5CO)_2NC(SCH_3) : NH$.—Twenty-five grams of the hydriodic acid salt of pseudomethylthiourea were dissolved in cold water and mixed with a concentrated solution of potassium hydroxide, containing 1 molecular proportion of the alkali (6.4 grams). To the solution were added, alternately, in small portions, 16.1 grams of benzoyl chloride and 6.4 grams of potassium hydroxide, which was previously dissolved in

water. The solution was kept cold by adding ice and was thoroughly shaken after each addition of the acid chloride and alkali. The diacylpseudothiourea separated as a curdy precipitate. After the odor of benzoyl chloride had disappeared the pseudothiourea was filtered off and the filtrate shaken again with 15 grams of benzoyl chloride and 8 grams of potassium hydroxide. We obtained practically as much more of the pseudothiourea as in the first treatment with benzoyl chloride. The product was washed with water and then triturated with ether, to remove any excess of benzoyl chloride. It melted at about 130°–135°, with slight evolution of methylmercaptan, solidified again, and then partially melted at 145°–146° to a semisolid, which gradually decomposed on heating and effervesced violently at 175°–185°. On account of the decomposition of the unsymmetrical derivative at its melting point, and the rapid change into the symmetrical form, it was impossible to obtain a sharp melting point of this compound. It is comparatively stable at ordinary temperatures, and is not rearranged to the symmetrical form by gentle treatment with 95 per cent alcohol. Some of the material that had been allowed to dry in the air for 20 hours was partially dissolved in hot alcohol, and the solution quickly filtered. The part that was not dissolved showed signs of melting at 135°, solidified again and then partially melted at 146°. Analysis:

	Calculated for $C_{16}H_{14}O_2N_2S$.	Calculated for $C_9H_{10}ON_2S$.	Found.
N	9.39	14.43	9.54

When the alcoholic solution (above) was quickly cooled, the unsymmetrical pseudothiourea deposited in the form of needles and showed the same behavior on melting as the original material. Analysis:

	Calculated for $C_{16}H_{14}O_2N_2S$.	Found.
N	9.39	9.69

Behavior with Alkali.—The unsymmetrical pseudothiourea was insoluble in alkali. Some of the urea was suspended in a cold, 20 per cent sodium hydroxide solution and allowed to stand at ordinary temperatures over night. When examined

the next morning, the pseudothiourea had dissolved with complete decomposition. The odor of methylthiocyanate was not detected.[1] When the alkaline solution was acidified with hydrochloric acid we obtained a crystalline precipitate, that deposited from hot water in plates and melted at 120°. It was identified as benzoic acid. In order to show that, by the treatment with alkali, one benzoyl radical had been removed with formation of benzoylpseudomethylthiourea, the alkaline solution, after filtering from benzoic acid, was treated as follows: It was made slightly alkaline with sodium hydroxide and shaken with a few grams of benzoyl chloride. A crystalline product was obtained which was identified as the unsymmetrical dibenzoylpseudomethylthiourea.

Behavior with Hydrochloric Acid.—When the unsymmetrical pseudothiourea was boiled with hydrochloric acid it was completely decomposed. It dissolved to a clear solution that deposited, on cooling, a crystalline compound which melted at 120°. It was identified as benzoic acid. When mixed with pure benzoic acid the melting point was not lowered. The hydrochloric acid solution was evaporated to dryness, and an oily residue was obtained which gave a strong test for sulphur. It did not solidify on long standing and was extremely soluble in alcohol. On account of the small amount produced it was not further examined.

Behavior on Heating.—Some of the unsymmetrical pseudothiourea was heated in a sulphuric acid-bath at 150°, for 20 minutes. There was a slight evolution of methylmercaptan. The crude product obtained did not show the same behavior as the original material when heated in a capillary tube. It melted at 146°–148°, without effervescence, to a turbid oil. It crystallized from alcohol in long, slender needles, which melted at 147°–148°, to a clear oil. A nitrogen determination agreed with the calculated for *symmetrical dibenzoylpseudomethylthiourea*, $C_6H_5CONHC(SCH_3) : NCOC_6H_5$.

	Calculated for $C_{16}H_{14}O_2N_2S$.	Found.
N	9.39	9.35

[1] Wheeler: *Loc. cit.*

This molecular rearrangement also took place when an alcohol solution of the unsymmetrical pseudothiourea was boiled for a long time. The symmetrical derivative deposited, on cooling, in needles and melted at 147°–148°, to a clear oil.

Behavior with Alkali.—The symmetrical dibenzoylpseudomethylthiourea dissolves, without decomposition, in a 20 per cent solution of sodium hydroxide. When the alkaline solution was acidified with dilute hydrochloric acid the symmetrical derivative was obtained, melting sharply at 147°–148°, to a clear oil. Analysis:

	Calculated for $C_{16}H_{14}O_2N_2S$.	Found.
N	9.39	9.3

Behavior with Hydrochloric Acid.—When the symmetrical dibenzoylpseudomethylthiourea was boiled with hydrochloric acid, methylmercaptan was evolved and it was converted, practically quantitatively, into symmetrical dibenzoylurea.[1] It was purified for analysis by crystallizing from acetic acid. It could be made to melt anywhere from 198° to 210°, according to the rate of heating and the size of the capillary tube used. Analysis:

	Calculated for $C_{15}H_{12}O_2N_2$.	Found.
N	10.44	10.41

Unsymmetrical Dibenzoylpseudoethylthiourea, $(C_6H_5CO)_2NC(SC_2H_5) : NH$.—This unsymmetrical derivative was obtained when pseudoethylthiourea was treated with benzoyl chloride, under the same conditions as in the preparation of the corresponding dibenzoylpseudomethylthiourea. We used the following proportions: Fifteen grams of the hydrobromic acid salt of pseudoethylthiourea, 22.6 grams of benzoyl chloride and 15.7 grams of potassium hydroxide. The reaction was perfectly smooth and the unsymmetrical derivative separated as an oil, which finally solidified, on continuous agitation. It was washed with cold alcohol and ether, and allowed to dry in the air. It partially melted at 104°–105°,

[1] Schmidt: J. prakt. Chem., [2], 5, 58.

then completely solidified in the capillary tube and melted, at 110°, to a clear oil, without effervescence. Analysis:

	Calculated for $C_{17}H_{16}O_2N_2S$.	Found.
N	8.97	8.97

Behavior with Alkali.—The unsymmetrical pseudothiourea was insoluble in a solution of sodium hydroxide. When the alkaline solution was warmed the pseudothiourea was decomposed, with formation of benzoic acid and monobenzoylpseudoethylthiourea. The benzoic acid was identified by its melting point, 120°. The monobenzoylpseudoethylthiourea separated as an oil which would not solidify.

Behavior with Hydrochloric Acid.—Some of the unsymmetrical pseudothiourea was boiled with 20 per cent hydrochloric acid, for 15 minutes. There was immediate decomposition, with formation of a crystalline product and an oil. The oil did not solidify on cooling and was, undoubtedly, monobenzoylpseudoethylthiourea. The crystalline material was filtered off and treated with a dilute solution of sodium hydroxide. A small proportion did not dissolve at once in the alkali and it was separated by filtration. It melted at 110° and was identified as symmetrical dibenzoylpseudoethylthiourea (see below). Its presence here is probably due to the fact that the unsymmetrical pseudothiourea was partially rearranged by the warm acid solution, before being decomposed by the hydrochloric acid. When the alkaline solution was acidified with hydrochloric acid we obtained an immediate precipitate of benzoic acid, which melted sharply at 120°.

Behavior on Heating.—The unsymmetrical derivative is rearranged at its melting point into *symmetrical dibenzoylpseudoethylthiourea*, $C_6H_5CONHC(SC_2H_5):NCOC_6H_5$. This symmetrical derivative was also easily obtained when the labile modification was crystallized from 95 per cent alcohol. It deposited in needles which melted, at 110°–111°, to a clear oil. Analysis:

	Calculated for $C_{17}H_{16}O_2N_2S$.	Found.
N	8.97	9.21

Behavior with Alkali.—The symmetrical dibenzoylpseudoethylthiourea is a weak acid. It gradually dissolved in an excess of cold, 20 per cent sodium hydroxide to a clear solution. When the alkaline solution was carefully neutralized with hydrochloric acid, the symmetrical derivative was recovered unaltered. It melted sharply at 110°, to a clear oil.

Behavior with Hydrochloric Acid.—When the symmetrical dibenzoylpseudoethylthiourea was boiled for a long time with hydrochloric acid, ethylmercaptan was evolved, and it was converted, quantitatively, into symmetrical dibenzoylurea.

Symmetrical Diparabrombenzoylpseudomethylthiourea, $BrC_6H_4CONHC(SCH_3) : NCOC_6H_4Br$.—To an aqueous solution of 10 grams of the hydriodic acid salt of pseudomethylthiourea was added a saturated solution of potassium hydroxide, containing 7.6 grams of the alkali. The alkaline solution was then mixed with 20.1 grams of parabrombenzoyl chloride, which was previously dissolved in benzene. The first addition of acid chloride produced a bulky, gelatinous precipitate. This gradually assumed a granular appearance as we continued to add the chloride, and the solution was thoroughly agitated. The crystalline product was washed with alcohol and dried at ordinary temperatures, in the atmosphere. It melted, when rapidly heated, at 175°–177°, with some effervescence. This effervescence suggested the presence of some unsymmetrical diparabrombenzoylpseudomethylthiourea. The material deposited from hot, 95 per cent alcohol in needles, that melted at 178°, with slight effervescence, to a turbid oil. Analysis :

	Calculated for $C_{16}H_{12}O_2N_2Br_2S$.	Found.
N	6.14	6.17

Behavior on Heating.—Some of the crude diparabrombenzoylpseudomethylthiourea was heated in a sulphuric acid-bath for 1 hour, at 175°. It melted to a turbid oil and very little ethylmercaptan was evolved. The oil solidified at once, on cooling, to a crystalline mass, which deposited from hot alcohol in needles. They melted at 177°–178° to a turbid oil, with only slight effervescence. When some of this material was

mixed with the crude diparabrombenzoylpseudomethylthiourea, melting at 175°–177°, the mixture melted at the same temperature, 175°–177°. Analysis:

	Calculated for $C_{16}H_{12}O_2N_2Br_2S$.	Found.
N	6.14	6.21

Behavior with Alkali. — Diparabrombenzoylpseudomethylthiourea did not show the same behavior towards sodium hydroxide as the dibenzoylpseudothioureas previously described. We could not conclude from its behavior towards alkali whether we were dealing with an unsymmetrical or a symmetrical derivative. It apparently underwent complete decomposition. The only product isolated in a state of purity was parabrombenzoic acid, melting at 250°–251°. The crude material, melting at 175°–177°, showed the same behavior towards alkali as did the pure crystallized material obtained after heating for 1 hour, at 175°.

Behavior towards Hydrochloric Acid.—The pseudothiourea was very stable in presence of acids. It was recovered unaltered after boiling with hydrochloric acid for a long time. When it was boiled with hydrobromic acid it behaved as a symmetrical derivative. The crude product, melting at 175°–177°, and the material obtained after heating in a sulphuric acid bath at 175°, were both converted, practically quantitatively, into symmetrical diparabrombenzoylurea, with evolution of methylmercaptan. It was difficultly soluble in alcohol and acetic acid and decomposed, with effervescence, at 228°–233°, according to the rate of heating. Analysis:

	Calculated for $C_{15}H_{10}O_3N_2Br_2$.	Found.
N	6.57	6.47

Parabrombenzoylurea, $BrC_6H_4CONHCONH_2$.—This urea was prepared by heating 3 grams of parabrombenzoyl chloride with 0.8 gram of urea at 150°–155°, for 2.5 hours. It was difficultly soluble in alcohol and water. It deposited from water in microscopic crystals that melted at 236°–237°, with effervescence. Analysis:

	Calculated for $C_8H_7O_2N_2Br$.	Found.
N	11.52	11.48

Paramethoxybenzoylpseudomethylthiourea, $CH_3OC_6H_4CONHC(SCH_3) : NH$.—This pseudothiourea was prepared as follows: Ten grams of the hydriodic acid salt of pseudomethylthiourea were dissolved in water, with an excess of potassium hydroxide. To this alkaline solution was then added a benzene solution of 7.8 grams of anisyl chloride. The reaction proceeded slowly, and it was necessary to shake for a long time before the odor of anisyl chloride disappeared. Sufficient benzene was added to dissolve all the pseudourea formed. After the reaction was complete the benzene solution was dried over calcium chloride, and then allowed to evaporate spontaneously. We obtained a beautiful deposit of colorless, slender prisms that melted, at 103°–105°, to a colorless oil. They were very soluble in alcohol. Analysis:

	Calculated for $C_{10}H_{12}O_2N_2S$.	Found.
N	12.50	12.45

Symmetrical Diparamethoxybenzoylpseudomethylthiourea, $CH_3OC_6H_4CONHC(SCH_3) : NCOC_6H_4OCH_3$.—When pseudomethylthiourea was treated, in aqueous solution, with 2 molecular proportions of anisyl chloride and the calculated quantity of potassium hydroxide, it reacted to form a crystalline product that partially melted and decomposed at 145°–150°. This material was very impure, and was probably a mixture of the monoanisylpseudothiourea and the unsymmetrical and symmetrical dianisylpseudothioureas. Some of the substance was dissolved in warm alcohol. On cooling, needles deposited which melted sharply, to a clear oil, at 159°–160°. Analysis:

	Calculated for $C_{18}H_{18}O_4N_2S$.	Found.
N	7.82	7.91

Behavior with Hydrochloric Acid.—When the symmetrical pseudothiourea, melting at 159°–160°, was boiled with hydrochloric acid, mercaptan was evolved. It was converted, quantitatively, into dianisylurea that melted at 205°–207°, with de-

composition. The urea was difficultly soluble in alcohol, water and acetic acid. Analysis :

	Calculated for $C_{17}H_{18}O_3N_2$.	Found.
N	8.58	8.37

When the crude material, melting at 145°–150°, was boiled with hydrochloric acid, we obtained a large amount of dianisylurea, melting at 205°–207°. Accompanying this urea was also a small amount of crystalline material which melted at 170°–175°. This was not examined.

NEW HAVEN, CONN.,
January 3, 1906.

SOME NEW APPARATUS.

BY S. F. ACREE.

A New Form of Alkali Apparatus.

The only excuse for adding another alkali apparatus to the large number already before the chemical world is the fact that not one of those on the market absorbs carbon dioxide rapidly enough to enable us to make combustions accurately, in the common form of furnace, within the period of 1 hour. At the beginning and end of the combustion the carbon dioxide is greatly diluted with air or oxygen, and when this mixture is passed rapidly through the alkali apparatus, some of the carbon dioxide may escape the solvent action of the alkali solution. In the analysis of many compounds the burning must be done slowly, and in such cases the absorption of the carbon dioxide in the alkali apparatus is nearly complete. But in the analysis of substances which burn very smoothly, the writer has found that the great loss of time is that required, not for burning the substance, but for the complete collection of the carbon dioxide. Morse and Taylor,[1] however, have devised a combustion furnace in which the products of combustion are very little diluted with air and oxygen and, as a consequence, the carbon dioxide is much more nearly completely absorbed by any of the common forms of alkali apparatus in a shorter

[1] THIS JOURNAL, 33, 591.

time. Any improvement in the efficiency of an alkali apparatus is, consequently, of great value.

The writer has, therefore, made use of the stability of the Soxhlet alkali apparatus and the fine absorptive efficiency of glass wool, saturated with potassium hydroxide solution, as exhibited in the Wetzel[1] apparatus and has had one constructed according to Fig. I. The outer vessel contains two inner bulbs,

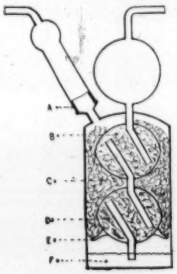

Fig. I.

B and D, connected as in Soxhlet's apparatus. These bulbs are filled with glass wool. Four small glass projections, E, extend from the lower bulb nearly to the wall of the outer vessel; these serve to hold fast the glass wool C, which is wound around the bulbs B and D. The calcium chloride tube, with a ground-glass joint at A, completes the apparatus. When the potassium hydroxide solution is introduced into the vessel, the glass wool inside and outside the bulbs becomes saturated at once with the liquid; the mixture of gases from the combustion tube must filter through all this glass wool and is exposed to such a large surface of alkali solution that the carbon dioxide is practically completely absorbed.

The apparatus can be made in any size desired. The writer uses one $4\frac{1}{2}$ inches high and $1\frac{3}{4}$ inches in diameter. When

[1] Ber. d. chem. Ges., **36**, 161.

filled with 50 per cent potassium hydroxide solution, so that the glass wool is saturated and the exit tube from the lower bulb dips into the liquid F, the apparatus weighs 60–65 grams. Not only is the absorption very good, but the apparatus is simple and is not easily broken, a very important point with the student beginning combustion work. The writer has made 8 combustions in one furnace, in a continuous period of 12 hours, by using 2 absorption apparatus.

The efficiency is illustrated by the following tests: During a period of 15 minutes nearly pure carbon dioxide was passed into 2 of these potash bulbs in series; the first one increased in weight nearly 1 gram, but the second did not gain as much as 0.10 milligram. A second experiment was made by passing a stream of gas, consisting of one-third carbon dioxide and two-thirds air, through the series; the first apparatus gained 0.20 gram, but the second one less than 0.10 milligram. A large number of combustions have been made in periods of time varying from 30 minutes to 1 hour, the results, in general, being very satisfactory. The writer feels that the apparatus can be relied upon to absorb the carbon dioxide as rapidly as substances can be safely and completely burned in any combustion furnace.

A Porcelain Lined Bomb for General Laboratory Use.

This bomb has been found to be of such general service in the laboratory that the writer wishes to let others know of its usefulness.

In Fig. II. the bomb E, is made of soft steel, tested to 250 atmospheres water pressure; the wall is approximately $\frac{3}{8}$ inch thick. The white porcelain lining F, has a thickness of $\frac{1}{16}$ inch and can be made of acid-proof or alkali-proof material; it covers the entire inner surface up to the threads at the neck of the bomb. The stopper B, is made of hard bronze, has a square head and screws into the neck of the bomb with heavy threads. The ring C, which is made either of very hard rubber or of lead, makes a gas-tight joint when the stopper is screwed down firmly. The valve consists of the hand-wheel I, attached to the screw A, on a square head. The screw fits

into the stopper with gas-tight threads and packing, shown only roughly in the figure. The screw has a tip D, that can be made of very hard rubber or of lead ; this closes the open-

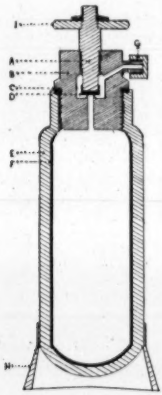

Fig. II.

ing into the bomb so that liquid carbon dioxide cannot escape from the apparatus. If it is desired, this tip D, can be replaced by one of the needle valve style. The inlet (outlet) G, has a cap and is threaded to fit carbon dioxide cylinders ; this threading can, of course, be made to order. The bomb rests in a ring base H, which can be removed readily.

The apparatus can be made in any size. The ones in use in this laboratory are about 10 inches in total height, 3 inches in outside diameter, and hold 430 cc. The mouth is 1½ inches in diameter and allows the easy introduction or removal of the substances to be used in the bomb.

The writer had this form of bomb made for use in experiments in which dry, liquid carbon dioxide was allowed to react with other substances in absolute ether. A piece of Manasse steel tubing, 1 inch outer diameter and 2 feet long,

properly threaded and tested to 100 atmospheres gas pressure, is used to connect the bomb to the carbon dioxide cylinder. This steel tube is filled with a long layer of calcium chloride next to the cylinder and a short layer of phosphorus pentoxide next to the bomb. When the bomb is cooled with salt and ice 100 grams of carbon dioxide can be introduced into it in 10 minutes, and the liquid is so nearly free from water that bright sodium wire is hardly affected by it in a week. When closed tightly, the bomb has stood 2 months, containing 100 grams of liquid carbon dioxide, without losing 1 gram.

The use of ether in the apparatus for 1 year has not appreciably affected the hard rubber ring and tip C and D, but it is certainly preferable to have these made of lead if organic solvents are to be used in the bomb, or if the apparatus is to be subjected to high temperatures.

It is evident that such a bomb is very serviceable for storing small quantities of gases, such as sulphur dioxide, ammonia, etc., that liquefy only under pressure or at low temperatures. The apparatus is convenient for use in the study of reactions in which gases are liberated; they can be drawn off at will and examined.

The bomb has proved to be especially serviceable in place of sealed tubes. The substances which are to react are introduced into the bomb, which is closed by means of a vise and a wrench. The heating is carried out in a water- or oil-bath. Substances which it is desired to mix in the bomb, after the latter has been closed, may be placed, in the usual manner, in thin-walled glass tubes, which are subsequently broken.

Apparatus for Rapid Precipitations in Electrolytic Analysis.

The apparatus is shown in Fig. III. K is a round, platinum gauze electrode, 2.5 inches in diameter. It consists of an outer ring forming one piece with the arm G, and an inner, removable ring which holds the gauze in position. The two rings can be held firmly together by means of fine platinum wire or 4 small drops of gold; it was found that the gold was

hardly affected by the solutions. The gauze is made of number 30 platinum wire, and there are 50 meshes to the linear inch. The arm G, is of number 16 platinum wire and is held

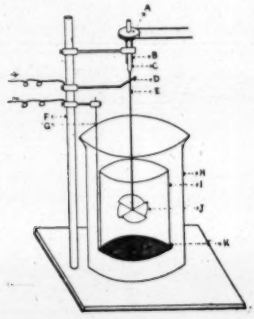

Fig. III.

in position by a binding post attached to the glass rod F, The electrode K, is kept ½ inch from the bottom of the beaker H, and supports the glass cylinder I, which has the same diameter as K, and, therefore, rests on the outer ring of K. The cylinder I, is completely submerged, the upper edge being at least ½ inch under the surface of the liquid. It is better to have several cylinders I, of various heights, to correspond to different volumes of liquid to be electrolyzed. The rotating, propeller-like electrode J, is made of heavy platinum foil and is riveted to the platinum rod E. E is sealed into the glass tube C, which is rotated in the glass tube B, by means of the pulley A, and a Rabe water turbine or a small electric motor. A platinum strip or a number 16 wire D, brushes against E, under the solution, and is connected to a binding post on F; this contact between D and E is excellent. The distance between K and J depends entirely upon the required voltage and the strength of the current to be used, and can be regulated at will. The beaker H, rests on the base of the

stand, or upon an asbestos board on a ring fitted to F if the solution is to be heated by a small burner.

The new and important feature of this apparatus is that the rotating disk J, forces all of the solution downward through the gauze K, up between the walls of H and I, and back down through K again. All of the liquid is thus brought close to the electrode K, as frequently as is wished.

At the end of the analysis the rotation of J is stopped, but the passage of the current continued; the liquid is siphoned out between H and I, while distilled water, or any other desired liquid, is poured into I. In this way the electrolyzed solution is easily removed without danger of the loss of the precipitated metal.

The conditions of voltage, current, temperature, etc., used in this apparatus are essentially those given in any good textbook, such as Classen's "Electrolytic Analysis."

This form of electrolytic apparatus was first made and used by the writer in the University of Utah, in 1901. At that time Perkin's[1] article describing his use of gauze electrodes had not appeared. The one described above is as simple in construction as any illustrated by Perkin, and has the decided advantage that the rotating electrode has excellent electrical contact without recourse to the expensive rotator used by him. The most important feature of this apparatus, however, and one which differentiates it from any yet described, is that all of the solution to be electrolyzed is forced by the rotating electrode into contact with the gauze as often as is wished, and the metal is more rapidly precipitated.

The apparatus has proved to be of great service in the rapid estimation of all the common metals, such as copper, silver, etc., and is especially useful in those analyses in which a metallic oxide—that of lead or of molybdenum[2]—is precipitated on the gauze. Analyses have often been made in 30 minutes in this apparatus, whereas the duplicate, electrolyzed in a beaker with a platinum cone or in a platinum dish, required 1–2 hours. Copper and lead dioxide are precipitated on

[1] Chem. News, 88, 102.

[2] Smith and Kollock: J. Am. Chem. Soc., 23, 669.

K in a hard coating, and very rarely in the spongy layer so often formed on a dish when the analysis is made too rapidly. The apparatus has proved to be as satisfactory in the hands of students, as regards accuracy of analysis, as platinum dishes, and a great saving of time is effected. The electrode is easily cleaned, dried and weighed, and the gauze is not readily injured. The cost is very much less than that of a platinum dish of 100 cc. capacity. The use of this electrode is especially advantageous with dilute solutions; the liquid can be electrolyzed directly, without evaporating it to the small volume necessary when dishes are used.

In the analysis of lead solutions it was found better to slip a piece of narrow, thin glass tubing, nearly the length of G, over this arm and fuse it to G close to K; in this way the precipitate was confined to K and the lead dioxide was afterwards dried by heating the electrode at 180°, in a beaker.

Any of the pieces of apparatus described in this paper can be purchased from Messrs Eimer and Amend.

JOHNS HOPKINS UNIVERSITY,
January 1, 1906.

ON THE FORMATION OF ALCOHOLATES BY CERTAIN SALTS IN SOLUTION IN METHYL AND ETHYL ALCOHOLS.

[FIFTEENTH COMMUNICATION.]

BY HARRY C. JONES AND LEROY MCMASTER.

It was shown by Jones and Getman[1] that a large number of salts have the power to combine with water when dissolved in that solvent. Indeed, this property is possessed by salts in general, although in very different degrees. Those salts that have the greatest power to combine with water as water of crystallization, have, as a rule, the greatest power to combine with water in aqueous solution.

Having established this fact in aqueous solutions, the question naturally arose, do salts have the power to combine with

[1] THIS JOURNAL, 31, 303 (1904).

any solvent other than water when dissolved in the solvent in question?

To throw light on this point, some work was carried out by Jones and Getman,[1] using ethyl alcohol as the solvent, and lithium chloride and nitrate, and calcium nitrate as the dissolved substances. In still earlier work Jones and Getman[2] used ethyl alcohol as the solvent, and potassium iodide, sodium iodide, ammonium iodide, cadmium iodide and sodium bromide as the dissolved substances.

The results show, in general, that the molecular rise of the boiling point of the solvent produced by the dissolved substance is greater than the theoretical molecular rise for ethyl alcohol, either as found by direct experiment in dilute solutions of non-electrolytes in the solvent in question, or as calculated by the equation

$$C = \frac{2\,T^2}{100\,L}.$$

In a number of the above cases very marked differences manifest themselves—differences which are far too large to be accounted for on the basis of the dissociation of the dissolved substance.

Take the case of lithium chloride in ethyl alcohol, as worked out by Jones and Getman.[3] The molecular rise of the boiling point is not only greater than the theoretical rise at nearly all of the concentrations employed, taking into account, of course, the dissociation; but the molecular rise increases rapidly with the concentration of the solution. Thus from 0.07 N to 2.07 N the molecular rise of the boiling point produced by lithium chloride increases, with a fair degree of regularity, from 1.28 to 2.43. As the concentration of the solution increases the dissociation, of course, decreases, and this would tend to cause the molecular rise to decrease with increasing concentration.

[1] THIS JOURNAL, **32**, 338 (1904).
[2] *Ibid.*, **31**, 338 (1904).
[3] *Ibid.*, **32**, 339 (1904).

Notwithstanding this influence, we have just seen that the molecular rise increases rapidly with increase in the concentration of the solution. Since, in the preparation of the solutions, both solvent and dissolved substance were taken in weighed quantities, the question of the change in the specific gravity of the solutions does not come into play.

Jones and Getman[1] interpreted their results by the boiling point method, in ethyl alcohol as the solvent, in the same manner that they had previously interpreted their results by the freezing point method in aqueous solutions. The abnormally great rise in the boiling point of ethyl alcohol, produced by certain salts, was due to combination between the dissolved substance and part of the solvent—to the formation of alcoholates in solution. The part of the alcohol which was in combination with the dissolved substance would thus be removed from the field of action as far as solvent is concerned. There being less alcohol present acting as solvent, the rise in the boiling point produced by the dissolved substance would be, of course, greater than if all the alcohol was playing the rôle of solvent.

This suggestion accounts for the facts in the case of solutions in alcohol, just as the hydrate theory had explained the abnormally great lowering of the freezing point of water produced by a large number of salts, especially when the concentrations were great.

The object of the present investigation is to extend the earlier work of Jones and Getman to a larger number of salts, and to more than one non-aqueous solvent. We have repeated the work, in ethyl alcohol, with a few of the same substances that were employed by Jones and Getman, and have added a number of others to the list of those that were earlier studied.

We have worked with lithium chloride, lithium bromide and lithium nitrate in methyl alcohol; and with lithium chloride, lithium bromide, lithium nitrate and calcium nitrate in ethyl alcohol.

In making the boiling point measurements, the boiling point apparatus of Jones[2] was employed. In order to be independent

[1] THIS JOURNAL, 32, 342 (1904).
[2] *Ibid.*, 19, 581 (1897).

of correction for changes in the barometer, two pieces of boiling point apparatus were used. In one of these the pure solvent was boiled and in the other the solution.

The alcohols used in this work were dehydrated by the usual methods, and care was taken to keep them free from moisture when transferred to the boiling point apparatus. The conductivity of the methyl alcohol, at 25°, was 2×10^{-6}, and that of the ethyl alcohol from 1 to 2×10^{-6}. The salts were all completely freed from water.

The usual precautions were taken in making the boiling point measurements, and the proper correction applied for the solvent that existed in the apparatus in the form of vapor. The top of the condenser was closed by means of a tube filled with calcium chloride, to prevent the moisture in the air from coming in contact with the alcohol in the boiling point apparatus.

In the following tables m is the concentration in terms of gram-molecular normal. This was obtained by dividing the number of grams of salt in 1000 grams of the solvent by the molecular weight of the salt; ρ is the corrected rise in the boiling-point of the solvent, produced by the dissolved substance at the concentration in question; $\frac{\rho}{m}$ is the molecular rise in the boiling point of the solvent at the given concentration.

The results for lithium chloride, bromide and nitrate are given in Tables I. to III. Calcium nitrate, in methyl alcohol, could not be satisfactorily studied on account of its limited solubility in this liquid.

Results with Methyl Alcohol.

The constant for methyl alcohol is 0.84. By comparing with this value, the molecular rise found, we can see at once the magnitude of the discrepancy between the value obtained experimentally and the theoretical value for an undissociated substance. All three of the following salts are, of course, disso-

ciated to a greater or less extent by methyl alcohol. This, however, would scarcely account for the magnitude of the molecular rise even in the most dilute solutions, since the dissociating power of methyl alcohol is only from one-third to one-half that of water. Dissociation is entirely incapable of accounting for the ***increase in the molecular rise with increase in the concentration of the solution*** which, we see from the results, takes place in the case of all three of the above salts. The dissociation would decrease with increase in the concentration, which would tend to diminish the magnitude of the molecular rise of the boiling point as the solutions became more and more concentrated.

Attention should also be called to the ***magnitude of the molecular rise*** in the most concentrated solutions employed. In such solutions it is almost ***twice*** the boiling point constant, or normal molecular rise for this solvent. The dissociation in such solutions is certainly not greater than between 30 and 40 per cent.

Table I.—Lithium Chloride in Methyl Alcohol.

m.	ρ.	$\frac{\rho}{m}$.
0.0453	0.061	1.34
0.1050	0.140	1.33
0.1377	0.181	1.31
0.2404	0.313	1.30
0.2598	0.340	1.31
0.2891	0.380	1.31
0.3188	0.424	1.33
0.3965	0.529	1.33
0.4557	0.610	1.34
0.4921	0.660	1.34
0.4964	0.670	1.35
0.5762	0.779	1.35
0.6919	0.973	1.40
0.7522	1.068	1.42
0.7717	1.100	1.42
0.7961	1.139	1.43
0.8635	1.250	1.44
0.9258	1.347	1.45
1.0074	1.512	1.50
1.1847	1.838	1.55

Table II.—Lithium Bromide in Methyl Alcohol.

m.	ρ.	$\frac{\rho}{m}$.
0.0919	0.129	1.40
0.1409	0.192	1.36
0.1780	0.241	1.35
0.1970	0.270	1.36
0.2514	0.344	1.37
0.2557	0.351	1.37
0.2727	0.377	1.38
0.3101	0.412	1.33
0.3689	0.499	1.35
0.5554	0.756	1.36
0.6108	0.846	1.38
0.6182	0.858	1.38
0.6654	0.927	1.39
0.5882	0.808	1.37
0.6745	0.965	1.43
0.8571	1.287	1.50
1.2128	1.970	1.62

Table III.—Lithium Nitrate in Methyl Alcohol.

m.	ρ.	$\frac{\rho}{m}$.
0.0961	0.120	1.24
0.1369	0.163	1.19
0.1437	0.171	1.19
0.1711	0.202	1.18
0.2089	0.248	1.18
0.2367	0.286	1.21
0.2830	0.354	1.25
0.3744	0.475	1.26
0.4454	0.568	1.27
0.4504	0.575	1.27
0.4709	0.607	1.28
0.5300	0.684	1.29
0.6122	0.792	1.29
0.7338	0.976	1.33
0.7538	1.004	1.33
0.8342	1.132	1 35
0.9212	1.265	1.37
1.1320	1.563	1.38

We interpret these results in terms of the same theory that was advanced by Jones[1] in connection with aqueous solutions. There is combination between the solvent and the dissolved substance, forming, in the case of water, *hydrates*; in the case of alcohol, *alcoholates* in solution. As the concentration of the solution becomes greater, more and more alcohol is held in combination by the dissolved substance, consequently, there is less and less alcohol acting as solvent and the molecular rise in the boiling point, therefore, increases.

Results with Ethyl Alcohol.

The results in ethyl alcohol, obtained with lithium chloride, lithium bromide, lithium nitrate and calcium nitrate are given in Tables IV. to VIII.

We obtained results of the same general character as those found by Jones and Getman for the substances with which they worked in ethyl alcohol. The constant for ethyl alcohol is 1.15. If we examine the results for lithium chloride, bromide and nitrate, we shall find the molecular rise in the boiling point, especially in the more concentrated solutions, to be much greater than this value. Further, the molecular rise increases with the concentration of the solutions. The results

Table IV.—Lithium Chloride in Ethyl Alcohol.

m.	ρ.	$\frac{\rho}{m}$.
0.1356	0.191	1.408
0.3692	0.555	1.503
0.3958	0.595	1.503
0.5084	0.765	1.504
0.5350	0.803	1.500
0.5407	0.812	1.502
0.6478	1.025	1.582
0.6771	1.080	1.595
0.7577	1.218	1.607
0.8083	1.320	1.633
0.8235	1.347	1.635
0.8529	1.401	1.642
0.9035	1.495	1.650

[1] THIS JOURNAL, 23, 103 (1900).

Table V.—Lithium Bromide in Ethyl Alcohol.

m.	ρ.	$\frac{\rho}{m}$.
0.0762	0.096	1.276
0.1942	0.300	1.544
0.3390	0.514	1.516
0.3544	0.530	1.495
0.4387	0.675	1.538
0.5731	0.914	1.594
0.5892	0.945	1.604
0.6072	0.978	1.610
0.6280	1.000	1.629
0.7640	1.263	1.653
1.0336	1.935	1.872
1.0510	1.923	1.875
1.0530	1.981	1.881
1.1030	2.134	1.940
1.1730	2.325	1.982

Table VI.—Lithium Bromide in Ethyl Alcohol (Second Series).

m.	ρ.	$\frac{\rho}{m}$.
0.1126	0.140	1.24
0.1890	0.270	1.45
0.3815	0.550	1.44
0.4161	0.617	1.48
0.4476	0.665	1.48
0.5788	0.880	1.52
0.6513	1.031	1.58
0.7031	1.151	1.63
0.8312	1.441	1.73
0.9950	1.798	1.81
1.3142	2.655	2.02

Table VII.—Lithium Nitrate in Ethyl Alcohol.

m.	ρ.	$\frac{\rho}{m}$.
0.0815	0.103	1.280
0.1423	0.187	1.314
0.2990	0.421	1.407
0.3088	0.435	1.408
0.3234	0.459	1.420
0.3370	0.479	1.420
0.5377	0.776	1.440
0.6297	0.920	1.460
0.7330	1.072	1.460
0.7962	1.165	1.460
0.8444	1.241	1.470
1.1770	1.800	1.530
1.2530	1.951	1.557

Table VIII.—Calcium Nitrate in Ethyl Alcohol.

m.	ρ.	$\frac{\rho}{m}$.
0.0428	0.057	1.33
0.0594	0.078	1.31
0.1137	0.135	1.18
0.1153	0.138	1.19
0.1981	0.239	1.20
0.2161	0.253	1.17
0.2590	0.300	1.16
0.2920	0.333	1.14
0.2964	0.340	1.14
0.3081	0.351	1.14
0.3380	0.383	1.13
0.3486	0.395	1.13
0.3815	0.425	1.11
0.3978	0 444	1.11
0.5361	0.582	1.08
0 5680	0.620	1.09
0 6862	0.740	1.08
0.7029	0.750	1.07
0.8274	0.885	1.07
0.9118	0.972	1.06

in the more dilute solutions in ethyl alcohol might be partially explained on the basis of dissociation, since ethyl alcohol has about one-fourth the dissociating power of water. Dissociation, however, is incapable of explaining the magnitude of the molecular rise in the more concentrated solutions, and is entirely incapable of explaining the fact that the molecular rise of the boiling point increases with the concentration of the solution, up to the most concentrated solutions that were employed.

Calcium nitrate is an exception to the above relations, as was found earlier by Jones and Getman.[1] This was rather surprising, so we repeated the work and obtained essentially their results. The molecular rise in the boiling point of ethyl alcohol, produced by calcium nitrate, decreases, with a fair degree of regularity, from the most dilute to the most concentrated solution studied. In the most concentrated solutions the molecular rise becomes less than the theoretical value, 1.15, notwithstanding the fact that in such solutions we have quite appreciable dissociation. The conclusion to which we seem to be forced by the results is that calcium nitrate in ethyl alcohol is somewhat polymerized. We probably have also combination between the solvent and the salt, but this is more than overcome, as far as the effect on boiling point is concerned, by the polymerization of molecules of the salt itself, forming more complex aggregates than would be expressed by the simple formula $Ca(NO_3)_2$.

The conclusion to which we are led by the results, in general, in ethyl alcohol, is the same as that to which we have already referred in the case of solutions in methyl alcohol. The large value of the molecular rise in the more concentrated solutions would indicate that a part of the alcohol was not playing the rôle of solvent, but was combined with the dissolved substance. This would also account for the increase in the molecular rise of the boiling point with increase in the concentration of the solution, notwithstanding the fact that the dissociation is decreasing as the solution becomes more concentrated. As the amount of dissolved substance present in-

[1] THIS JOURNAL, **32**, 338 (1904).

creases, the total amount of the solvent combined with it increases, and less and less alcohol is acting as solvent as the concentration becomes greater and greater. This is in keeping with the law of mass action. The amount of the solvent combined with 1 molecule of the dissolved substance is probably greater the more dilute the solution, at least up to a certain point. We have not yet been able to work out even the approximate composition of the alcoholates formed, as Jones and Getman[1] and Jones and Bassett[2] have done in the case of aqueous solutions. This is due, in part, to the fact that we have not yet had time to determine accurately the dissociation of the various salts at the different dilutions in the alcohols. When such data shall have been secured, there ought to be no very serious difficulty in calculating the approximate composition of the alcoholates formed by the various salts in solution in these solvents. Work is now in progress on this and similar problems.

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RELATIVE RATES OF OXIDATION OF ORTHO, META AND PARA COMPOUNDS.

BY HAMILTON BRADSHAW.

In 1887 Dreyfus[3] determined the rate at which various organic compounds are oxidized by potassium permanganate. If n grams of a substance are required to reduce a quantity of potassium permanganate equal to that reduced in the same length of time by 1 gram of ethyl alcohol, then $1/n$ expresses, in a manner, the relative rate of oxidation of the substance. Dreyfus made his measurements in acid solution and used a very dilute solution of potassium permanganate, 1 cc = 0.0001 gram of crystallized oxalic acid. He found that the value of $1/n$ for the substances which he studied varies from 0.2 to 10,000. With the dihydroxybenzenes the rates of oxidation are in the ratio—ortho : meta : para : : 5000 : 2000 : 3333. For

[1] THIS JOURNAL, **31**, 303 (1904); **32**, 308 (1904). Z. physik. Chem., **49**, 385 (1904).
[2] THIS JOURNAL, **33**, 334 (1905).
[3] Compt. rend., **105**, 523.

the toluidines he found the ratio—ortho : meta : para : : 17.8 : 9.09 : 12.5.

The present investigation was undertaken, at the suggestion of President Remsen, to determine the rates of oxidation of certain isomeric organic compounds of the ortho, meta and para series. It was thought that a comparison of the behavior of several groups of such isomeric compounds might possibly reveal some tendency which would admit of general expression.

The compounds which were studied for this purpose are all easily prepared. Those that were obtained from the laboratory stock were purified by crystallization or distillation. The following is a list of the substances used, together with their melting-points (uncorr.):

	Melting point.
Salicylic acid	155°–156°
m-Hydroxybenzoic acid	198°–199°
p-Hydroxybenzoic acid	210°
Anthranilic acid	145°
m-Aminobenzoic acid	173°
p-Aminobenzoic acid	186°
o-Nitrophenol	45°–46°
m-Nitrophenol	95°–96°
p-Nitrophenol	112°–113°
o-Nitraniline	73°–74°
m-Nitraniline	112°
p-Nitraniline	147°
o-Toluidine	
m-Toluidine	
p-Toluidine	45°

Parahydroxybenzoic acid was made by fusing parasulphaminebenzoic acid with a mixture of sodium and potassium hydroxides.

Of all these substances, except the nitranilines, aqueous solutions were made, containing 1 gram to the liter. Only 0.5 gram of the nitranilines was dissolved in a liter of water, on account of the slight solubility of these compounds, but twice as much of the solution was used in each experiment. The

toluidines were dissolved by adding sufficient sulphuric acid to form the neutral salts. The solution of potassium permanganate used for the oxidations contained 4 grams of potassium permanganate to a liter of water. The procedure was as follows: A fixed amount of the solution of the organic substance was diluted to a definite volume and a quantity, usually 15 cc., of the solution of potassium permanganate was added from a burette. After allowing the mixture to stand for a certain length of time, the excess of potassium permanganate was determined. At first this was done by adding an excess of a solution of manganous sulphate, free from iron, and filtering off the precipitated oxides of manganese on an asbestos plug. By dissolving in a known quantity of a standard solution of oxalic acid, or of ferrous ammonium sulphate, and titrating the excess of reducing substance, the amount of available oxygen in the precipitate was determined, and, by subtraction, the oxygen used in the oxidation of the organic compound.

It was found, however, that this method does not give satisfactory results, probably on account of a loss of oxygen in heating the solution to dissolve the oxides of manganese. The method finally decided upon for the determination of the unreduced potassium permanganate, is that based on the liberation of iodine from potassium iodide by potassium permanganate, in the presence of an acid. At the end of the oxidation period an excess of a solution of potassium iodide and dilute hydrochloric acid was added to the mixture and the liberated iodine determined by titration with a solution of sodium thiosulphate, previously standardized against the solution of potassium permanganate by the same method.

In the case of the nitranilines the end product was not very definite. Apparently some oxidation product continued to liberate iodine and, consequently, the quantity of thiosulphate used was too great, although the titrations were made as rapidly as possible. The figures expressing the amounts of potassium permanganate reduced are, therefore, uniformly low for this group of compounds.

The oxidations were made at room temperature, which varied from 18° to 22°.

Hydroxybenzoic Acids.

The first group studied was that of the hydroxybenzoic acids. Measurements were made on solutions to which neither acid nor alkali had been added. The results are given in tabular form. In this and the following tables the quantity of potassium permanganate, reduced by the organic substance, is expressed as cubic centimeters of solution. For the sake of convenience, the reduction is regarded as being complete, that is, to the manganous condition.

Table I.—Oxidation of Hydroxybenzoic Acids.

0.005 gram $C_7H_6O_3$, 15 cc. $KMnO_4$, total volume 100 cc.

	$KMnO_4$ reduced, cc.		
Time in minutes.	Ortho.	Meta.	Para.
1	. .	0.46	0.24
2	1.37	0.94	0.37
5	1.85	1.50	0.69
10	2.23	1.99	1.27
20	2.75	2.57	1.91
30	3.18	2.83	2.37
60	3.51	3.47	3.37
120	3.86	4.53	4.64
1080	5.50	6.00	6.22

Numerous other experiments were made, varying the quantity of substance, of potassium permanganate and of water. The general result was always the same, that is, the ortho compound was most readily oxidized, the para compound least readily. The differences were, in a few cases, greater than those tabulated above, but were of the same general character. The effect of a greater excess of permanganate is very slight, unless its concentration be increased.

Complete oxidation of the hydroxybenzoic acids according to the equation

$$C_7H_6O_3 + 14O = 7CO_2 + 3H_2O,$$

would require for 0.005 of acid, 0.053 gram of potassium permanganate, yielding its oxygen according to the equation

$$2KMnO_4 + H_2O = 2KOH + 2MnO_2 + 3O.$$

The quantity of solution used, 15 cc., contained 60 milligrams of potassium permanganate.

A study was also made of the effect of the addition of varying amounts of acid or alkali to the solution. The results are brought together in Table II. The first column contains the number of equivalents of acid or alkali added to the solution. For example, the addition of 2 equivalents of acid or alkali means the addition of 1 molecule of sulphuric acid or 2 molecules of potassium hydroxide for every molecule of hydroxybenzoic acid in the solution.

Table II.—Oxidation of Hydroxybenzoic Acids.

0.005 gram $C_7H_6O_3$, 15 cc. $KMnO_4$, total volume 100 cc.

	$KMnO_4$ reduced, cc.					
	Ortho.		Meta.		Para.	
	2 min.	5 min.	2 min.	5 min.	2 min.	5 min.
20 acid	.	5.40	. .	5.80	. .	4.99
4 "	4.57	5.04	. .	5.27	. .	2.89
2 "	3.47	3.90	. .	4.00	. .	1.93
0 "	1.37	1.85	0.94	1.50	0.37	0.69
1 alkali	0.51	0.65	0.25	0.40	0.20	0.37
2 "	0.17	0.50	3.65	4.07	1.79	2.99
4 "	0.63	1.35	3.90	4.28	1.62	2.87
10 "	1.70	. .	3.53	. .	1.22	. .
20 "	2.36	3.05	3.30	3.96	1.15	1.59

In order to determine whether the effect of the addition of potassium hydroxide depends on the actual quantity of alkali in the solution, or on its concentration, measurements were made on solutions diluted with varying quantities of water. In the following table the figures at the head of the columns refer to the total volume of the solution.

Table III.—Oxidation of Hydroxybenzoic Acids.

0.005 gram $C_7H_6O_3$, 15 cc. $KMnO_4$, time 2 minutes.

	$KMnO_4$ reduced, cc.				
	Ortho.		Meta.		
	50 cc	100 cc.	50 cc.	100 cc.	150 cc.
1 acid	. .	. .	3.07	. .	. .
0 "	2.34	1.37	1.96	0.94	0.37
1 alkali	1.44	0.51	4.16	0.25	0.14
2 "	1.63	0.17	4.34	3.65	0.24
4 "	1.89	0.63	4.43	3.90	3.20
6 "	2.23	. .	4.42	. .	. .
10 "	. .	1.70	. .	3.53	. .
12 "	2.84	. .	. .	. .	. .
20 "	. .	2.36	. .	3.30	2.61

A careful study of these results leads to the conclusion that the effect of the alkali depends on its concentration in the solution, and not on the actual quantity present. For example, in the first column the point of minimum oxidation corresponds to the presence of a carboxyl salt, while in the second column the same point is reached only when sufficient alkali is present to form a neutral salt.

By separate experiments it was shown that sodium hydroxide has exactly the same effect as potassium hydroxide, and that the presence of corresponding quantities of potassium or sodium chloride has no influence whatever on the rate of oxidation.

During the process of oxidation the solution becomes alkaline, unless the potassium hydroxide, formed by the reduction of the potassium permanganate, is neutralized by acid oxidation products of the organic substance. It was found that considerable quantities of oxalic acid are formed when salicylic acid is oxidized by potassium permanganate. Acetic acid is known to be a frequent oxidation product of aromatic compounds. In view of the uncertainty arising from these facts, and also from a consideration of the results presented in Table II., it seemed more satisfactory to start with solutions made alkaline by the addition of considerable quantities of potassium

hydroxide. Table IV. contains the results obtained by oxidation in alkaline solution.

Table IV.—Oxidation of Hydroxybenzoic Acids.

0.005 gram $C_7H_6O_3$, 15 cc. $KMnO_4$, 10 equivalents KOH, total volume 100 cc.

	$KMnO_4$ reduced, cc.		
Time in minutes.	Ortho.	Meta.	Para.
2	1.70	3.53	1.22
10	3.25	4.70	2.39
30	4.66	5.25	3.93
60	5.34	5.50	5.02

Aminobenzoic Acids.

Table V.—Oxidation of Aminobenzoic Acids.

0.005 gram $C_7H_7O_2N$, 15 cc. $KMnO_4$, total volume 100 cc.

	$KMNO_4$ reduced, cc.		
Time in minutes.	Ortho.	Meta.	Para.
0.5 (at 0°)	1.35	1.24	0.73
1	2.18	2.26	1.59
2	2.41	2.73	1.92
15	2.81	3.67	3.47
340	3.58	4.89	4.89

The first three measurements were made at 0° because the experiments with the hydroxybenzoic acids show that the ortho compound is most readily oxidized in the first stages of the oxidation. These results with the aminobenzoic acids are exactly analogous to those obtained with the hydroxybenzoic acids. Further measurements were made in alkaline solution.

Table VI.—Oxidation of Aminobenzoic Acids.

0.005 gram $C_7H_7O_2N$, 15 cc. $KMnO_4$, 10 equivalents KOH, total volume 100 cc.

	$KMnO_4$ reduced, cc.		
Time in minutes.	Ortho.	Meta.	Para.
2	1.90	2.78	1.12
10	3.33	4.67	2.29
30	4.91	6.17	4.28
60	5.94	6.75	4.88

Here also, as with the hydroxybenzoic acids, the order of velocities is, meta, ortho, para.

Berkeley[1] found that the rate of reduction of the nitrobenzoic acids by stannous chloride increases from the meta to the para compound. His results seem to harmonize very satisfactorily with the conclusions reached in the present investigation.

Nitrophenols.

The nitrophenols being easily obtained, experiments were tried with them.

Table VII.—Oxidation of Nitrophenols.

0.005 gram $C_6H_5O_3N$, 15 cc. $KMnO_4$, total volume 25 cc.

	$KMnO_4$ reduced, cc.		
Time in minutes.	Ortho.	Meta.	Para.
1	1.05	0.78	0.36
5	2.25	1.75	0.68
30	5.60	5.15	3.01

Table VIII.—Oxidation of Nitrophenols.

0.005 gram $C_6H_5O_3N$, 20 cc. $KMnO_4$, total volume 30 cc.

	$KMnO_4$ reduced, cc.		
Time in minutes.	Ortho.	Meta.	Para.
90	6.24	6.20	5.90
390	6.80	6.51	6.72

Table IX.—Oxidation of Nitrophenols.

0.05 gram $C_6H_5O_3N$, 15 cc. $KMnO_4$, 10 equivalents KOH, total volume 50 cc.

	$KMnO_4$ reduced, cc.		
Time in minutes.	Ortho.	Meta.	Para.
10	0.42	1.84	0.30
30	1.12	3.27	0.35
60	1.51	4.33	0.69
120	2.15	4.67	0.91

The results with solutions of the free nitrophenols are similar to those obtained for the two preceding groups. Here also, in alkaline solution, the order of velocities is meta, ortho, para.

[1] Dissertation, Johns Hopkins University, 1899.

Nitranilines.

Table X.—Oxidation of Nitranilines.

0.005 gram $C_6H_6O_2N_2$, 15 cc. $KMnO_4$, total volume 25 cc.

	$KMnO_4$ reduced, cc.		
Time in minutes.	Ortho.	Meta.	Para.
10	0.22	2.94	0.22
60	0.91	4.04	0.43
10 (at 100°)	5.08	5.82	3.15

Table XI.—Oxidation of Nitranilines.

0.005 gram $C_6H_6O_2N_2$, 15 cc. $KMnO_4$, 10 equivalents KOH, total volume 35 cc.

	$KMnO_4$ reduced, cc.		
Time in minutes.	Ortho.	Meta.	Para.
30	1.12	4.23	0.84
60	1.35	4.52	0.89
120	2.53	4.91	1.22
360	3.02	5.19	1.71

Both of these tables show the same order in the rates of oxidation of the nitranilines, namely, meta, ortho, para.

Toluidines.

Table XII.—Oxidation of the Toluidines.

0.005 gram C_7H_9N, 15 cc. $KMnO_4$, 10 equivalents KOH, total volume 100 cc.

	$KMnO_4$ reduced, cc.		
Time in minutes.	Ortho.	Meta.	Para.
0.5	3.94	4.28	2.55
1	4.28	4.75	2.72
2	4.69	5.13	3.03
5	5.30	5.61	3.51

In acid solution the oxidation was rapid and nearly equal for all 3 isomers.

In all 5 groups a uniformity is shown only in alkaline solution. The differences in the rates of oxidation of isomeric

substances are quite marked and the rate of oxidation decreases from the meta to the para compound.

JOHNS HOPKINS UNIVERSITY,
June, 1905.

ORTHOSULPHAMINEBENZOIC ACID AND RELATED COMPOUNDS.

BY HAMILTON BRADSHAW.

A few years ago F. D. Wilson, working in the laboratory of the Johns Hopkins University, made a comparative study of orthosulphaminebenzoic acid, $C_6H_4\begin{cases}COOH\\SO_2NH_2\end{cases}$, and orthocarbaminebenzenesulphonic acid, $C_6H_4\begin{cases}CONH_2\\SO_2OH\end{cases}$.[1] As a few points were left unsettled I have continued the work at the suggestion of President Remsen.

Wilson states that orthosulphaminebenzoic acid crystallizes in two forms, plates and needles, and that the quantity of alkali used in the hydrolysis of the benzoic sulphinide determines which form the acid will take on crystallization. Several experiments were made to test this point. Wilson boiled a solution of 20 grams of benzoic sulphinide with 15 grams of sodium hydroxide, in 500 cc. of water, until hydrolysis was complete. The solution was acidified and allowed to stand over night. Large, monoclinic crystals were deposited. In repeating this work it was found that complete hydrolysis was not reached even after 15 hours' boiling. After cooling and filtering, the solution was acidified with hydrochloric acid. Only needles were deposited. Another alkaline solution, obtained in exactly the same way, was divided into two portions. One part of it was acidified and allowed to stand. Both forms of crystals began to appear, but on agitating the solution the plates ceased to form and the acid came down in needles. The second portion was acidified and seeded with plate crystals. All of the acid was deposited in the form of plates. In an-

[1] THIS JOURNAL, 30, 353 and Dissertation.

other experiment Wilson used 10 grams of benzoic sulphinide to 20 grams of sodium hydroxide and 250 cc. of water. This solution, treated in the same way as the previous one, gave only needles, the yield being almost quantitative. In the first experiment in which these proportions were used, Wilson's conclusions were confirmed, that is, only needles were obtained. In the second, a few plate crystals formed among the needles. Moreover, it was found that this proportion of alkali caused complete hydrolysis in less than 3 hours.

To determine whether the presence of benzoic sulphinide would induce the formation of plate crystals, the next solution of the hydrolyzed benzoic sulphinide was divided into two portions. To one, benzoic sulphinide was added until the solution tasted sweet. When acidified, the solution deposited most of the acid in needles, only a few plates being formed. The second portion of solution, containing no benzoic sulphinide, yielded only large plate crystals. From these experiments it is evident that the form of the crystals does not depend on the quantity of alkali used, nor on the presence of benzoic sulphinide. It is very probable that the plate crystals are formed only when the acidified solution suffers the least possible disturbance. Similar relations are known to hold with many other substances.

As stated by Wilson, the plate form of the acid contains no water of crystallization, while the needle crystals lose 0.5 molecule of water of crystallization at 100°–110°.

	Calculated for $C_6H_4(COOH)SO_2NH_2.\frac{1}{2}H_2O$.	Found. I.	Found. II.
H_2O	4.29	4.33	4.25

When crystallized from alcohol the acid is deposited in large rhombohedrons. Another form of crystals was obtained by hydrolyzing 20 grams of benzoic sulphinide with 30 grams of potassium hydroxide, in 500 cc. of water. When acidified, the solution deposited the acid in small, irregular crystals, about 1–2 mm. in diameter. The study of the crystalline form was not considered to be of sufficient importance to justify further investigation. The melting point of the acid, in whatever form it may be crystallized, is 152° (uncorr.).

Orthosulphaminebenzoic acid loses water when heated and is converted, at least partially, into benzoic sulphinide. A portion is probably converted into acid ammonium orthosulphobenzoate, as is the case with parabromorthosulphaminebenzoic acid.[1] Wilson states that in a rapid current of air the needles decompose at 115°, the plates at about 128°, and that, in a closed tube, the needles decompose at 145°, the plates at 135°.

In repeating this work, an apparatus was used similar to that described by Wilson, but the thermometer was placed in the glass tube with the boat, and windows of mica were fixed in the outer casing, to permit the reading of the thermometer and accurate observation of the decomposition. The crystals were powdered before being placed in the boat. It was found that both needles and plates became sweet when heated at 114°–116°, for 2 hours, either in a rapid current of air or in a closed tube. Very little water collected in the cool part of the tube. Generally a slight sublimate of benzoic sulphinide was noticed.

Wilson's Diamide.

Wilson prepared what he supposed to be the diamide, $C_6H_4\begin{cases}CONH_2\\SO_2NH_2\end{cases}$, by heating orthosulphaminebenzoic acid with ammonium thiocyanate. By following his directions carefully, a product was obtained which melted at 256°–257° (uncorr.). Wilson gives 263°. It is very soluble in water, insoluble in cold alcohol, more soluble in hot alcohol. It gives off ammonia when treated in the cold with a solution of sodium hydroxide. These facts indicated that the substance is ammonium orthocarbaminebenzenesulphonate.[2] A determination of nitrogen completed the evidence:

0.2450 gram salt gave 0.0315 gram N.

	Calculated for $C_6H_4(CONH_2)SO_3ONH_4$.	Found.
N	12.86	12.85

[1] Blanchard: THIS JOURNAL, 30, 509.
[2] Wilson: *Loc. cit.*, p. 370.

Orthocarbaminebenzenesulphonic Acid.

Potassium orthocarbaminebenzenesulphonate was prepared as directed by Wilson. When this salt is heated with phosphorus oxychloride, a compound is obtained which Wilson supposed to be orthocarbaminebenzenesulphone chloride. He crystallized it from chloroform and found the melting point to be 63°. By the action of phosphorus pentachloride on the same salt, Sohon[1] obtained orthocyanbenzenesulphone chloride, which he identified by converting it into orthocyanbenzenesulphonic acid. It seemed very probable that the reaction with phosphorus oxychloride would give the same product. The chloride was prepared as directed by Wilson, and crystallized from chloroform. It melts at 69°–70° (uncorr.). The same substance was then prepared by the action of phosphorus oxychloride on potassium orthocyanbenzenesulphonate. This salt was obtained from the ammonium salt which is formed by the action of ammonia on the unsymmetrical chloride of orthosulphobenzoic acid.[2] The chloride obtained in this way melted at 69°–70°. Jesurun[3] prepared the same chloride by heating benzoic sulphinide with 2 molecules of phosphorus pentachloride, in a sealed tube, at 70°–75°. He gives the melting point as 69°–70°. Specimens of the chloride prepared by all three of these methods were found to have the some melting point, 69°–70°, which was not lowered by mixing one specimen with another. There is no doubt, therefore, that the action of phosphorus oxychloride includes dehydration of the carbamide group,

$$C_6H_4(CONH_2)SO_2OK \rightarrow C_6H_4(CN)SO_2Cl.$$

This explains Wilson's failure to obtain the diamide,

$$C_6H_4\begin{cases}CONH_2\\SO_2NH_2\end{cases},$$

by the action of ammonia on the chloride which he supposed to be orthocarbaminebenzenesulphone chloride. Jesurun[4] de-

[1] THIS JOURNAL, **20**, 271.
[2] *Ibid.*, **30**, 268.
[3] Ber. d. chem. Ges., **26**, 2288.
[4] *Ibid.*, **26**, 2296.

scribes the action of ammonia on orthocyanbenzenesulphone chloride as follows: If an excess of ammonia is used the product is pseudosaccharin amide, $C_6H_4\begin{cases}C(NH)\\ SO_2\end{cases}N$, melting above 300°. If the chloride is treated with benzene, in which the theoretical quantity of ammonia has been dissolved, the product is orthocyanbenzenesulphonamide, $C_6H_4\begin{cases}CN\\ SO_2NH_2\end{cases}$, melting above 260°. This work was repeated, using the chloride obtained by Wilson's method, and Jesurun's results were confirmed, except in regard to the melting points. Pseudosaccharin amide, when crystallized from hot water, melts at 297° (uncorr.). Analyses:

I. 0.2025 gram substance gave 0.0310 gram N.
II. 0.1722 gram substance gave 0.0267 gram N.
III. 0.2118 gram substance gave 0.2742 gram $BaSO_4$.

	Calculated for $C_6H_4\begin{cases}C(NH_2)\\ SO_2\end{cases}N$.	Found. I.	II.
N	15.38	15.30	15.49
S	17.59	. .	17.60

Orthocyanbenzenesulphonamide melts at 160° (uncorr.), changing completely, at its melting point, to the isomeric substance, pseudosaccharin amide, which melts at 297° (uncorr.). If heated rapidly no melting is observed at 160°. This explains Jesurun's observation that the substance melts above 260°.

When orthocyanbenzenesulphonamide is heated with a dilute solution of sodium hydroxide it is converted into benzoic sulphinide. It may be that the diamide is first formed and loses ammonia immediately. The diamide has not yet been prepared.

Anilineorthosulphonic Acid.

This acid can be prepared by the action of sodium hypobromite on an alkaline solution of potassium orthocarbaminebenzenesulphonate. Forty grams of this salt and 32 grams of

sodium hydroxide were dissolved in 320 cc. of water. The solution was warmed to 80° on the water-bath, and 28 grams of bromine, dissolved in 220 cc. of a 10 per cent solution of sodium hydroxide, were added drop by drop. The mixture was heated about 15 minutes and, after cooling, was acidified with hydrochloric acid. By evaporating to a very small bulk and filtering while hot, the sodium chloride was removed. The anilineorthosulphonic acid crystallized out on cooling and was obtained pure by recrystallization from hot water. Analysis:

0.0927 gram substance gave 0.1255 gram $BaSO_4$.

	Calculated for $C_6H_4(NH_2)SO_3OH$.	Found.
S	18.51	18.58

If the sodium hypobromite is added rapidly to a cold solution of the carbamide, the chief product is tribromaniline. This is easily explained by the fact that anilineorthosulphonic acid is readily converted into tribromaniline by the action of free bromine.[1] If the sodium hypobromite is added slowly to a cold solution of the carbamide, the product is parabromanilineorthosulphonic acid. Even under the most favorable conditions some of this acid is formed. It is very insoluble in cold water and can be removed by filtration.

JOHNS HOPKINS UNIVERSITY,
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SOME DERIVATIVES OF PHENYLGLYCOCOLLORTHOSULPHONIC ACID.

BY HAMILTON BRADSHAW.

Anilineorthosulphonic Acid.

The preparation of this acid from orthocarbaminebenzenesulphonic acid has been described in the preceding article. This method, including the preparation of the carbamine acid, was too laborious for the production of the acid in any considerable quantity, and the method of Kreis[2] was tried, with good results. Acetanilide was brominated in glacial acetic acid

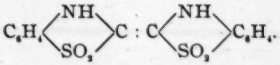
[1] Berndsen and Limpricht: Ann. Chem. (Liebig), **177**, 100 (1875).
[2] Ann. Chem. (Liebig), **286**, 377.

solution[1] and the product was crystallized from alcohol. The directions of Kreis were followed in the sulphonation of the parabromacetanilide. There was considerable charring and the yield was never better than 65 per cent of the theoretical. Any unchanged parabromaniline was removed by distilling an alkaline solution with steam. The bromine was removed by boiling with zinc dust and alkali.[2] Prolonged boiling was found to be necessary. After removing the zinc, the sulphonic acid was separated from the sodium chloride as described in the preceding paper. The identity of the substance was positively confirmed by diazotization and conversion into orthoethoxybenzenesulphonamide, $C_6H_4(OC_2H_5)SO_2NH_2$, melting at 156° (uncorr.).[3] On titration, 0.9 gram of the acid required 0.2914 gram of potassium hydroxide for neutralization, calculated 0.3919 gram.

Phenylglycocollorthosulphonic Acid.

It was desired to prepare a sulphonic acid corresponding to phenylglycocollorthocarboxylic acid and to condense it to a compound analogous to indigo, thus:

$$2C_6H_4(SO_2OH)NHCH_2COOH \rightarrow$$



Attempts were made to condense anilineorthosulphonic acid with chloracetic acid, just as anthranilic acid condenses with chloracetic acid.[4] The proportions used correspond to those recommended for anthranilic acid. Ten grams of anilineorthosulphonic acid, 6.5 grams of chloracetic acid and 10.5 grams of sodium carbonate were dissolved in 320 cc. of water and the solution boiled for several hours, under a return condenser. The original acid was recovered unchanged. The same result was obtained when no sodium carbonate was added. The two acids were then heated, in aqueous solution, in a sealed tube,

[1] Hübner: Ann. Chem. (Liebig), **209**, 355.

[2] Kreis: *Loc. cit.* Gerilowsky: Ber. d. chem. Ges., **29**, 1075.

[3] Franklin: THIS JOURNAL, **20**, 462.

[4] Mauthner and Suida: Monats. Chem., **9**, 728. Heumann: Ber. d. chem. Ges., **23**, 3432. German Imp. Pat., **56**, 273.

with and without the addition of sodium carbonate, at about 150°, for several hours. No evidence of condensation was detected. Bromacetic acid was then tried, with the same negative result. Similar attempts to condense sulphanilic acid with chloracetic acid also failed. Anthranilic acid condenses very readily. Orthonitraniline does not condense with chloracetic acid, but condenses readily with bromacetic acid.[1] The failure of the anilinesulphonic acids to condense with chloracetic acid is probably to be explained by the strongly negative character of the sulphonic acid group.

Phenylglycocollorthocarboxylic acid is easily prepared by the action of formic aldehyde and hydrocyanic acid on anthranilic acid, and hydrolysis of the resulting nitrile:[2]

$$C_6H_4(COOH)NH_2 + CH_2O + HCN = C_6H_4(COOH)NHCH_2CN + H_2O;$$

$$C_6H_4(COOH)NHCH_2CN \rightarrow C_6H_4(COOH)NHCH_2COOH.$$

There are two steps in the first process, the condensation with formic aldehyde and the subsequent addition of hydrocyanic acid, thus:

$$C_6H_4(COOH)NH_2 + CH_2O = C_6H_4(COOH)N:CH_2 + H_2O;$$

$$C_6H_4(COOH)N:CH_2 + HCN = C_6H_4(COOH)NHCH_2CN.$$

This method was found to be very satisfactory when applied to anilineorthosulphonic acid. The following proportions were found to give the best results: Aniline orthosulphonic acid, 8.65 grams, was dissolved in 50 cc. of hot water containing 3.25 grams of anhydrous potassium carbonate. Ten cc. of hydrochloric acid, sp. gr. 1.16 = 7.3 grams of HCl, were added, and then a concentrated solution of potassium cyanide, till the mixture became neutral to Congo red paper. It was now made slightly acid by means of a few drops of concentrated hydrochloric acid, whereupon 3.75 cc. of a 40 per cent solution of formic aldehyde were added and the mixture was warmed on the water-bath for about an hour. At the end of this time a concentrated solution of about 8 grams of potas-

[1] Plöchl: Ber. d. chem. Ges., 19, 7.

[2] German Imp. Pat., 117, 924; 120, 105.

sium hydroxide was added and the solution was boiled until evolution of ammonia ceased. After cooling, enough hydrochloric acid was added to precipitate the phenylglycocollorthosulphonic acid as the acid potassium salt, which is rather sparingly soluble in cold water. It dissolves in concentrated hydrochloric acid and the free sulphonic acid crystallizes out of the solution.

The materials from which this salt was obtained being comparatively difficult to prepare, most of the following experiments were made with parabromphenylglycocollorthosulphonic acid. This was prepared in exactly the same way as the bromine-free compound, 12.6 grams of parabromanilineorthosulphonic acid being substituted for the 8.65 grams of anilineorthosulphonic acid. The acid potassium salt obtained in this way is very insoluble in cold water. It was recrystallized from hot water, from which it is deposited in needles. The salt contains water of crystallization, but loses it in varying amounts when dried in the air. A determination of potassium was made on a portion dried at 125°.

0.2932 gram salt gave 0.0722 gram K_2SO_4.

	Calculated for $C_6H_3Br(SO_3OK)NHCH_2COOH$.	Found.
K	11.24	11.05

When a solution of this salt, in hot water, is rendered strongly acid with hydrochloric acid and allowed to cool slowly, the free sulphonic acid is deposited in flaky crystals. It is very soluble in water, much less soluble in a rather concentrated solution of hydrochloric acid. When titrated, 0.1119 gram required 0.0287 gram of sodium hydroxide for neutralization, calculated 0.0289 gram.

If the free acid, contaminated with potassium chloride, is dissolved in hot, absolute methyl alcohol, the solution filtered and evaporated to a rather small bulk, the acid is changed to an ester acid, which can be precipitated by the addition of ether. Analysis:

0.5841 gram substance gave 0.3369 gram AgBr.

	Calculated for $C_6H_3Br(SO_3OH)NHCH_2COOCH_3$.	Found.
Br	24.66	24.54

When titrated, 0.1708 gram of the ester acid required 0.0215 gram of sodium hydroxide for neutralization, calculated 0.0211 gram. The ester was saponified by boiling with an excess of a standard solution of sodium hydroxide. By titrating the excess of alkali, the amount consumed was determined. Total sodium hydroxide used for saponification and neutralization 0.0429 gram, calculated 0.0422 gram.

Attempts at Condensation.

1. Phenylglycocollorthocarboxylic acid is converted into indigo by fusing with sodium hydroxide at 250°–300°, dissolving the resulting mass in water and passing air through the solution.[1] Since fused alkali at this high temperature replaces the sulphonic acid group by phenolic hydroxyl, this method of condensation was not tried on parabromphenylglycocollorthosulphonic acid.

2. Phenylglycocoll is converted into indigodisulphonic acid by the action of fuming sulphuric acid.[2] Phenylglycocollorthocarboxylic acid gives no indigo by this method, but it seemed desirable to try it on the corresponding sulphonic acid. Accordingly, 15 grams of acid potassium parabromphenylglycocollorthosulphonate were added, slowly, to 50 grams of fuming sulphuric acid, containing 20 per cent free sulphuric anhydride, the temperature being maintained below 40°. A considerable quantity of gas was evolved during the process of solution. The mixture was added to 100 grams of fuming sulphuric acid containing 80 per cent free sulphuric anhydride and allowed to stand for half an hour. The acid was then poured on ice. A white solid separated, which, on crystallization from hot water, was found to be parabromanilineorthosulphonic acid. Analysis:

0.5693 gram substance gave 0.4297 gram AgBr.

[1] Heumann: Ber. d. chem. Ges., 23, 3432.

[2] Heumann: *Ibid.*, 24, 1476, 3070. German Imp. Pat., 63, 218; 68, 372.

	Calculated for $C_6H_3Br(NH_2)SO_3OH$.	Found.
Br	32.11	31.71

0.3025 gram required 0.0478 gram sodium hydroxide for neutralization, calculated 0.0480 gram.

The fuming sulphuric acid removes the acetic acid portion of the molecule and probably oxidizes it to oxalic acid, which, of course, would appear as carbon monoxide and carbon dioxide. When phenylglycocollorthosulphonic acid is treated with fuming sulphuric acid it evolves gas just as the bromine derivative does.

3. Diacetylindoxyl, $C_6H_4\begin{cases}N(C_2H_3O)\\ C(OC_2H_3O)\end{cases}\!\!>\!\!CH$, is very easily prepared by heating the neutral sodium salt of phenylglycocollorthocarboxylic acid with acetic anhydride.[1] Carbon dioxide is evolved during the reaction and the product is insoluble in water. It is easily converted into indigo by boiling with dilute alkali. This method of condensation was tried on parabromphenylglycocollorthosulphonic acid by boiling 5 grams of the acid potassium salt with 1.5 grams of anhydrous sodium acetate and 25 grams of acetic anhydride for some time, under a return condenser. No carbon dioxide was evolved during the reaction. The acetic anhydride was distilled off under reduced pressure. The residue was very soluble in water. The solubility of the product, and the fact that no carbon dioxide was evolved made it seem very probable that the substance obtained was still a sulphonic acid and that the reaction had not gone beyond the acetylation of the imino group.

4. The neutral esters of phenylglycocollorthocarboxylic acid are very easily converted into esters of indoxylic acid by the action of sodium alcoholates.[2] Attempts were made to prepare neutral esters of parabromphenylglycocollorthosulphonic acid by the action of methyl iodide on the silver salt of the acid methyl ester, and by the action of dimethyl sulphate on the neutral sodium salt of the acid, but without success. No

[1] German Imp. Pat., 113, 240.
[2] Vorländer and Schilling: Ann. Chem. (Liebig), 301, 349.

further attempts were made in this direction, as the condensation probably depends on the presence of the carbonyl group, like all Claisen condensations.

5. Sodamide has been used recently in place of sodium hydroxide in the preparation of indoxyl and indoxylic acid from phenylglycocollorthocarboxylic acid.[1] The application of this method to the sulphonic acid gave some promise of success, because the temperature required is lower, and the disturbing influence of the fused alkali on the sulphonic acid group is practically eliminated. The sodamide was prepared by the method of Dennis and Browne.[2] No condensation product could be obtained, however, when acid potassium parabromphenylglycocollorthosulphonate was heated at about 200° with the sodamide, or at 250° with the sodamide diluted with potassium cyanide.

These methods, used in the preparation of indigo from phenylglycocollorthocarboxylic acid, having failed when applied to the corresponding sulphonic acid, further attempts to effect the condensation did not seem to be justified.

I desire to express my thanks to President Remsen for suggesting this problem to me.

JOHNS HOPKINS UNIVERSITY,
June, 1905.

ON DERIVATIVES OF FORMHYDROXAMIC ACID AND THE POSSIBLE EXISTENCE OF ESTERS OF FULMINIC ACID. II.

BY H. C. BIDDLE.

It was suggested some time ago by Nef[3] that the esters of fulminic acid might result by the elimination of hydrogen chloride from the esters of chloroformyloxime (formylchloridoxime). In the preceding paper[4] I discussed the synthesis and general properties of methylchloroformoxime and called attention to the peculiar isonitrile-like odor which is produced when a solution

[1] German Imp. Pat., 137, 955.
[2] J. Am. Chem. Soc., 26, 587.
[3] Ann. Chem. (Liebig), 280, 340 (1894).
[4] THIS JOURNAL, 33, 60 (1895).

of this ester in ether or ligroin is treated with potassium hydroxide. It was thought at the time that the odor might be due to the formation of methyl fulminate.

As a continuation of the work has been somewhat retarded by the difficulty of securing material, the complete study of the reaction has only been recently effected.

The liquid remaining after evaporating the ether, or ligroin, was distilled under diminished pressure. From a preliminary analysis of the colorless distillate and a determination of its molecular weight, I was at first disposed to consider that I was dealing with the ester $(CH_3ONC)_2$.

Subsequent study of the reaction, however, has shown that the substance under consideration was really methyl diiminooxalate, $HN:C(OCH_3)C(OCH_3):NH$, and that, in the action, of potassium hydroxide on methyl chloroformoxime, there is produced not only this body but also, among other products, methyl cyaniminocarbonate, $HN:C(OCH_3)CN$, and the potassium salts of hydrocyanic, cyanic and oxalic acids. It is evident that no molecular rearrangement of the molecule of methyl fulminate will account for these reaction products and it is equally evident that their occurrence points to the complete disruption of the molecule of methyl chloroformoxime.

In an attempt to account for these unexpected results we may note that the primary action which we should naturally expect would be expressed by the simple equation :

$$CH_3ON:CHCl + KOH \rightarrow CH_3ON:C + KCl + H_2O.$$

It is highly probable that the fulminic ester thus occurs as an intermediate product, but, if so, its instability under the conditions of the experiment evidently precludes its isolation.

If it were immediately dissociated we should naturally expect, as dissociation products, carbon monoxide or formic acid and methyl hydroxylamine. The presence of traces of potassium formate in the alkaline residue points to a slight dissociation in this direction.

On the other hand, the fulminic ester, being unsaturated, might condense to form the double molecule,

$$CH_3ON : C : C : NOCH_3,$$

and this, in turn, suffering decomposition, might be dissociated simultaneously in two directions, in one case leading to the formation of oxalic acid and methyl alcohol, and in the other to the formation of cyanogen and methyl alcohol, according to the equation:

$$3(CH_3ONC)_2 + 4H_2O \rightarrow 6CH_3OH + H_2C_2O_4 + N_2 + 2C_2N_2.$$

Such twofold dissociation of the double molecule fully accounts for the occurrence of salts of hydrocyanic, cyanic and oxalic acids. It might be urged that the oxalic acid arises from the decomposition of the diiminooxalic ester, but, as shown by Nef,[1] diiminooxalic esters, in the presence of an alkali, under no condition yield derivatives of oxalic acid. This was fully confirmed in the case of the methyl ester by allowing it to stand in contact with solid potassium hydroxide for 24 hours. Not a trace of potassium oxalate was formed.

The occurrence of methyl alcohol and cyanogen serves fully to explain the formation of both cyaniminocarbonic ester and diiminooxalic ester in the reaction. As shown by Nef,[2] cyanogen, in the presence of an alcohol and in contact with an alkali, absorbs 1 and 2 molecules of the former, giving rise to the esters just named,

$$C_2N_2 + ROH \rightarrow HN : C(OR)CN + ROH \rightarrow HN : C(OR)C(OR) : NH.$$

Diiminooxalic methyl ester was synthesized and compared with the product obtained from the action of potassium hydroxide on methyl chloroformoxime. The methyl ester proved to be a crystalline solid, melting at 29°.5–30°.5. The product derived from methyl chloroformoxime was not obtained as a solid, but, as I shall show later, the failure to solidify was due to the presence of traces of cyaniminocarbonic ester, from which, with the small quantity at my command, 0.5 gram and less, it was found impossible to free it. As regards composi-

[1] Ann. Chem. (Liebig), 287, 284 (1895).
[2] *Ibid.*, 287, 223.

tion, constitution and general behavior towards reagents, the two esters proved to be absolutely identical.

From these results it seems highly improbable that the carbyloxime esters will ever be synthesized by as drastic a method as that involved in the elimination of hydrogen chloride from the esters of chloroformoxime. The pronounced tendency of the entire molecule to undergo dissociation under the conditions obtaining in the reaction naturally indicates the futility of all synthetic methods in which this dissociative tendency is not greatly diminished.

EXPERIMENTAL.

Action of Potassium Hydroxide on Methyl Chloroformoxime.— To a well cooled solution of 10 grams of methyl chloroformoxime, in absolute ether, is added, gradually, an excess of powdered potassium hydroxide. There arises immediately the isonitrile-like odor already referred to in the previous paper. The action, slight at first, is later accompanied by the evolution of small quantities of an inert gas, possessing the general negative properties of nitrogen. During the entire reaction the liquid remains perfectly free from any odor of ammonia. As soon as the completion of the action is indicated by the disappearance of the chloride from the solution, the ether is decanted from potassium salts, evaporated and the brown liquid remaining, less than 1 gram, is distilled under diminished pressure. There is thus obtained approximately 0.5 gram of colorless liquid, boiling at about 60° (25 mm.). The small amount of product naturally precluded an exact determination of the boiling point.

The residue in the distilling bulb, fully 0.3 gram, is converted into a resin at a higher temperature.

The colorless liquid was redistilled and analyzed :

0.1248 gram substance gave 0.1910 gram CO_2 and 0.0796 gram H_2O.

0.0787 gram substance gave 16.5 cc. moist N, at 13° and 752.3 mm.

	Calculated for $C_4H_8O_2N_2$.	Found.
C	41.46	41.73
H	6.90	7.08
N	24.12	24.6

A determination of the molecular weight was made by the freezing-point method, using benzene as solvent.

0.1079 gram substance in 17.44 grams of benzene gave a depression of 0°.285.

0.1361 gram substance in 17.44 grams of benzene gave a depression of 0°.360.

	Calculated for $C_4H_8O_2N_2$.	Found. I.	Found. II.
Mol. wt.	116	108.5	108.3

On treating the liquid with concentrated hydrochloric acid, it is saponified to methyl alcohol, ammonia and oxalic acid. Not a trace of methoxylamine or hydroxylamine is produced in this reaction.

Although not in a condition of absolute purity, the substance analyzed is, without doubt, methyl diiminooxalate. As will be shown later, its general properties fully identify it with this ester.

An examination of the mixture of salts resulting from the action of potassium hydroxide on methyl chloroformoxime showed the presence, in quantity, of potassium chloride, cyanide, cyanate, oxalate and carbonate, together with traces of potassium formate.

The cyanic acid was detected by the method suggested by Schneider.[1]

For the complete identification of the methyl diiminooxalate obtained above, attention was now turned to the direct synthesis of this body.

Methyl Diiminooxalate, $HN:C(OCH_3)C(OCH_3):NH$.—As shown by Nef,[2] the ethyl esters of cyaniminocarbonic acid and diiminooxalic acid are formed by conducting chlorine into a solution of potassium cyanide in water-alcohol, the course of the reaction, as he has indicated, being essentially as follows:

[1] Ber. d. chem. Ges., 28, 1540 (1895).
[2] Ann. Chem. (Liebig), 287, 296.

The cyanogen chloride produced is absorbed by potassium cyanide, forming the addition product, KNC(CN)Cl, which is then converted by the alcohol into cyaniminocarbonic ester. Under the influence of the alkali a portion of the latter body adds a second molecule of alcohol, thereby giving rise to diiminooxalic ester.

Since the methyl esters of cyaniminocarbonic acid and diiminooxalic acid had not been prepared, they were synthesized according to the general method given by Nef.

A somewhat rapid stream of chlorine is run into a solution of 50 grams of potassium cyanide in 300 grams of water and 100 grams of methyl alcohol, cooled to $-5°$–$0°$. As soon as the solution, which smells strongly of cyanogen chloride, becomes weakly alkaline or neutral, it is extracted with ether, the ether extract is washed 3 times with water to remove alcohol, and is then dried by calcium chloride. The brown oil remaining after distilling off the ether and cyanogen chloride, was fractionated under diminished pressure. It was thus separated into two parts, the larger portion boiling at $33°$–$34°$ and the lesser at $54°$–$55°$ (22 mm.) The latter soon solidified in the receiver to a mass of colorless, transparent plates.

The larger fraction, as shown by a nitrogen determination, is methyl cyaniminocarbonate,

$$HN : C(OCH_3)CN.$$

0.12 gram substance gave 33.7 cc. moist N_2 at 12° and 757.7 mm.

	Calculated for $C_3H_4ON_2$.	Found.
N	33.33	33.31

Methyl cyaniminocarbonate is a colorless, mobile liquid, boiling at $33°$–$34°$ (22 mm.). It possesses a peculiarly penetrating and irritating odor, somewhat resembling that of an isonitrile and practically identical with that noted during the early stages of the action of potassium hydroxide on methyl chloroformoxime. The substance is but slightly soluble in water. It cannot be kept for any length of time without undergoing marked decomposition.

Thus, if exposed to diffused sunlight for a few days, it is completely converted into a dark, resinous tar.

The smaller fraction, as shown by analysis, is methyl diiminooxalate, $HN : C(OCH_3)C(OCH_3) : NH$.

0.1593 gram substance gave 0.2418 gram CO_2 and 0.1000 gram H_2O.

0.0888 gram substance gave 18.4 cc. moist N_2 at 14° and 755.3 mm.

	Calculated for $C_4H_8O_2N_2$.	Found.
C	41.46	41.38
H	6.90	6.97
N	24.12	24.30

Methyl diiminooxalate crystallizes in colorless, transparent plates, melting at 29°.5–30°.5. It is characterized by a peculiar, sweetish odor, which is always noticed on the completion of the action of potassium hydroxide on methyl chloroformoxime. The substance is more stable than methyl cyaniminocarbonate, although, on standing, it is gradually converted into a dark resin.

Like its homologue, the ethyl ester, concentrated hydrochloric acid saponifies the methyl ester to methyl alcohol, ammonia and oxalic acid. If added to an excess of well cooled, dilute hydrochloric acid, 1 con. acid : 10 water, it is resolved into ammonia and methyl oxalate. On extracting the solution with ether and evaporating the latter, the methyl ester separates in characteristic crystals, melting at 54°.

Methyl diiminooxalate, as synthesized above, proved to be identical in every respect with the product obtained by the action of potassium hydroxide on methyl chloroformoxime, save in the fact that the latter did not solidify. It can scarcely be questioned that this failure to solidify is due to the contaminating presence of a trace of cyaniminocarbonic ester, which could not be separated from the small amount of substance obtained, about 0.5 gram.

This appears not only from the fact that the product derived from methyl chloroformoxime indicated, by a variable boil-

ing point, the presence of a lower boiling liquid, but also from the fact that, in one instance, in which an excess of potassium hydroxide was avoided, the substance resulting possessed the properties, such as boiling point, odor, etc., not of the diiminooxalic ester but of the cyaniminocarbonic ester.

It is evident, then, that in both syntheses, cyaniminocarbonic ester is first produced and that this, in the presence of the alkali, subsequently adds a molecule of alcohol to form the diiminooxalic ester.

As shown by Nef,[1] so pronounced is the tendency of ethyl cyaniminocarbonate to add alcohol in the presence of an alkali, that the ester and alkali alone suffice to give rise to diiminooxalic ester, the action depending on the partial decomposition, and the subsequent addition of the alcohol to unchanged cyaniminocarbonic ester:

$$HN : C(OC_2H_5)CN + 2KOH \rightarrow KNC + KOCN + C_2H_5OH + H_2O.$$

The tendency of the methyl ester to absorb a molecule of alcohol is equally pronounced, as is shown by the following experiment:

A somewhat rapid stream of chlorine was run into a solution of 50 grams of potassium cyanide in 300 grams of water and 100 grams of methyl alcohol, cooled to —5°–0°. As soon as the solution became neutral there was added to it a solution of 32 grams of potassium cyanide, in 50 grams each of methyl alcohol and water.

After standing for 6 hours, at 20°–30°, the mixture was diluted slightly with water and extracted with ether, as in the previous experiment.

The reaction product consisted almost entirely of diiminooxalic ester with a trace of cyaniminocarbonic ester.

[1] Ann. Chem. (Liebig), **287**, 282.

UNIVERSITY OF CALIFORNIA,
BERKELEY, CAL.,
Jan. 10, 1906.

Contributions from the Chemical Laboratory of the University of Illinois.

AMINE DERIVATIVES OF MESOXALIC ESTERS.

By Richard Sydney Curtiss.

In a former paper[1] the fact was noticed that many ineffectual attempts, by various investigators, have been made to link one and two amine groups to the methylene carbon in malonic esters, to form $H_2NCH(COOR)_2$ and $(H_2N)_2C(CO_2R)_2$. A saponification was always first effected and an amine formed whenever ammonia was allowed to act on the haloid esters:

$$X_{1-2}C(COOR)_2 \rightarrow X_{1-2}C(CONH_2)_2.$$

More recently Willstätter[2] has tried, unsuccessfully, to displace the two negative groups in ethyl bromnitromalonate, $NO_2CBr(CO_2C_2H_5)_2$, by the amino group, working with ammonia in alcohol, water and ether solutions. The bromine was eliminated and salts of the base with ethyl isonitromalonate are formed, $MON{<}^{O}_{}{>}C(CO_2C_2H_5)_2$.

The first successful results recorded in this line of work were those obtained when negatively substituted ammonias (aniline, etc.) were used with brominated malonic esters. In this manner ethyl anilinomalonate, $C_6H_5NHCH(CO_2C_2H_5)_2$, and ethyl dianilinomalonate, $(C_6H_5NH)_2C(CO_2C_2H_5)_2$,[3] as well as a series containing substituting groups in the benzene ring were made.[4] The only aminomalonic ester containing an amine group relatively more positive than ammonia has recently been made by the action of dimethylamine on methyldibrommalonate.[5] This resulted in the formation of methyl tetramethyldiaminomalonate, $[(CH_3)_2N]_2C(CO_2CH_3)_2$. O. Piloty and J. Neresheimer[6] have recently obtained ethyl aminomalonate.

[1] This Journal, 19, 691.
[2] Ber. d. chem. Ges., 34, 1775.
[3] This Journal, 19, 693, 698.
[4] *Ibid.*, 30, 133.
[5] Willstätter: Ber. d. chem. Ges., 38, 1378.
[6] *Ibid.*, 39, 514 (1906).

Some time ago,[1] while engaged in a study of the arylamine derivatives of ethyl malonate, the action of 2 molecules of aniline on a molecule of ethyl oxomalonate, $OC(CO_2C_2H_5)_2$, was tried. Heat was generated on mixing the substances and, after 24 hours, balls of long, prismatic crystals were found in the oil. This substance melted at 117°–118° (uncorr.), and agreed in this and other characteristics with ethyl dianilinomalonate, $(C_6H_5NH)_2C(CO_2C_2H_5)_2$, the product which is formed by the action of aniline on ethyl dibrommalonate.[2] This result, however, was not published at the time. Subsequently, Conrad and Reinbach[3] described the reactions between these two substances using, however, the free acid instead of its ester. They obtained dianilinomalonic acid from the aniline salt first produced and suggest that the esters may be so formed by the action of aniline on ethyl and methyl oxomalonate. Schmitt[4] has recently tried this reaction. His product of the action of aniline on ethyl mesoxalate called "bisanilide de mesoxalate d'ethyle" must be very impure, however, as he gives its melting point as 103°, whereas it really melts at 117°–118°[5] (uncorr.), when pure.

In like manner he has prepared methyl dianilinomalonate and gives its melting point as 113°.5. Conrad and Reinbach,[6] who first made this substance, found that it melted 11° higher, *viz.*, at 125°. No analytical figures accompany Schmitt's work. He has, apparently, overlooked both papers in which the properties of these two substances are described.

Petriew[7] studied the effect of an aqueous solution of ammonia on ethyl dihydroxymalonate. He obtained "yellow deliquescent crystals" of dihydroxymalonamide, $(HO)_2C(CONH_2)$. The ester was, therefore, saponified. I have succeeded in getting an action with dry ammonia gas on the ketone group in ethyl oxomalonate, $OC(CO_2C_2H_5)$, forming an unstable, addition

[1] THIS JOURNAL, 19, 701.
[2] *Ibid.*, 19, 695.
[3] Ber. d. chem. Ges., 35, 1820.
[4] Compt. rend., 141, 49.
[5] THIS JOURNAL, 19, 695. *Loc. cit.*
[6] J. russ. Chem. Ges., 10, 76. Beilstein: "Handbuch d. Org. Chem.," I, 1398.
[7]

product, $HN\langle^{COH(CO_2C_2H_5)_2}_{COH(CO_2C_2H_5)_2}$, while leaving intact the usually reactive ester part of the molecule.

The Action of Ammonia on Ethyl Dihydroxymalonate.

When studying the action of ammonia gas on ethyl dihydroxymalonate it was noticed that the results vary greatly with the conditions of the experiment. To obtain a fairly pure product a low temperature is necessary, as well as a properly chosen solvent and drier. Seven and six-tenths grams of pure ethyl dihydroxymalonate were dissolved in 120 cc. of dry benzene. To remove the water formed in the reaction about 70 grams of zinc chloride, in small sticks, were added, and immediately thereafter, ammonia gas, carefully dried over sticks of potassium hydroxide, was passed into this solution. The whole was kept at the freezing point of the solvent. Care was also taken to avoid atmospheric moisture entering the apparatus. After a few seconds the clear, colorless solution becomes cloudy, due to the separation of water. After 20 minutes this begins to disappear and in 2 minutes more the solution is again water-clear and the action is over. The increase in weight of the mass is about 3 grams. Toward the end of the operation a faint tint of yellow appears, due to an oily impurity which is very difficult to remove. If the operation is carried out at ordinary room temperatures this is largely increased. The solution is now allowed to stand for 10 minutes in the freezing mixture and then filtered from the encrusted zinc chloride. The benzene is removed from the clear filtrate by distillation from a water-bath at 50° (80 mm.); 6.8 grams of a yellowish-white, crystalline mass remain in the distilling flask. This was at once dissolved in 125 cc. of warm, dry ether and filtered from a little yellowish-white impurity. The solution was cooled in ice-water, and the crystals which separated on standing 15–20 minutes were filtered off. The ethereal filtrate is slightly opalescent. The formation of the substance which causes this increases slowly, hour by hour, in the solution, so

that it is necessary to crystallize quickly and avoid the moisture of the air coming in contact with the substance.

The new compound was recrystallized once or twice from dry ether, until the melting-point showed no change. It melts at 103°–105° on quickly heating; the melting point is not sharp, as it commences to decompose as soon as superficially melted. The colorless oil at first formed instantly begins to turn amber-yellow while giving off a colorless gas. If melted in a test tube, ammonia is given off in quantity at 105°–110°.

Analysis of the substance, recrystallized from dry ether and dried in a vacuum over solid potassium hydroxide :

I. 0.2494 gram substance gave 9.5 cc. N at 25° and 736.4 mm.

II. 0.2976 gram substance gave 10.2 cc. N at 24° and 756.3 mm.

III. 0.2252 gram substance gave 0.3832 gram CO_2 and 0.1237 gram H_2O.

	Calculated for $HN(COH(CO_2C_2H_5)_2)_2$	Found. I.	II.	III.
C	46.02	. .	. .	46.35
H	6.30	. .	. .	6.08
N	3.84	4.26	4.03	. .

The substance is ethyl dihydroxyiminodimalonate and appears to be formed by the substitution of the imine group in place of two hydroxyl groups in 2 molecules of ethyl dihydroxymalonate, $(HO)_2C(CO_2C_2H_5)_2$, or by direct addition of ammonia to the keto group in ethyl oxomalonate, from which it can also be made. It crystallizes from ether in flat, rectangular tablets ; if the solution be poured on a watch-glass, in beautiful, large, fern-like sprays. It is very easily electrified when rubbed with glass. It is insoluble in carbon bisulphide, slightly soluble in ligroin. It dissolves fairly well in ether, easily in benzene and acetic ether, very easily in acetone and chloroform. It is insoluble, as such, in cold water, but is, however, quickly decomposed by it. The solution in water smells strongly of ammonia and gives, on evaporation in a vacuum, ethyl dihydroxymalonate, m. p. 57°. It is dis-

sociated in the same manner, though more slowly, by standing in moist air, and also by solution in alcohol. It can be kept, when pure, in a desiccator over solid potassium hydroxide for weeks, without losing ammonia.

Phosphorus pentachloride (1. mol.), mixed with the crystals, generates heat and soon causes a semi solution, evolving large quantities of hydrogen chloride. The resulting product has not been fully investigated.

The study of the reactions of mesoxalic esters with ammonia derivatives and hydrazines will be continued.

URBANA, ILL.,
Feb. 24, 1906.

REPORTS.

The Oxidation of Atmospheric Nitrogen with Reference to the Manufacture of Nitrates and Nitric Acid.

(1) Die Nutzbarmachung des Luftstickstoffs. Rede, gehalten bei der Eröffnung des neuen technisch-chemischen Instituts der Königlichen technischen Hochschule zu Berlin, am 25ten November, 1905, Von dem Director des Instituts, Geheimer, Regierungsrat Prof. Dr. Otto N. Witt.[1]

(2) Ueber die Oxydation des Stickstoffes in der Hochspannungs-flamme. Von Johannes Brode, Ph.D., Privatdozent für physikalische Chemie und Electrochemie an der Technischen Hochschule zu Karlsruhe, Baden. Halle: Wilhelm Knapp. 1905. 63 pp. Price, M. 2.50.

Prof. Witt's speech and Dr. Brode's monograph together cover the subject; the former is a popular description of the Birkeland-Eyde process, is illustrated by diagrams and photographs, and may be considered authoritative, as the inventors were present. The latter goes deeper into the subject of nitrogen oxidation, and includes investigations of high-tension flames by Brode and by others, giving, also, minuter details of the technical processes than does Witt.

We owe the first experiments on the oxidation of atmospheric nitrogen to Cavendish,[2] who, in 1781, noticed that the water formed by burning hydrogen in an excess of air contains nitric acid, and in 1786[3] showed that all of the nitrogen in a volume of air can be burned if enough oxygen is added and

[1] Chem. Indus., **28**, 699, 1905.
[2] Thorpe: "Essays in Historical Chemistry," p. 83.
[3] Phil. Trans., **75**, 372.

energy enough supplied in the form of electric sparks; a small bubble of gas always remained unburned, as Cavendish observed, which bubble Rayleigh,[1] repeating the experiment 100 years later, showed to be argon. Priestley made observations similar to those of Cavendish at about the same time.[2] Spottiswoode,[3] in 1880, found that, under certain conditions, the discharge of an alternating current with high potential, in air, is not in the form of sparks or of an arc, but has the form of a perfect flame. Subsequent attempts to utilize the Cavendish reaction have little technical or scientific interest till 1895, when Naville and Guye[4] showed that where there is a certain concentration of nitrous gases in contact with the sparks, the ratio of oxidation to energy employed lessens greatly; hence, oxidized air should be instantly removed from the sparking space; it must not be passed through again, and the sparking chamber should be as small as possible, to hinder diffusion of oxidized air into the fresh air entering. In the same year Lord Rayleigh and Sir William Ramsay discovered argon, and Rayleigh,[5] repeating the Cavendish experiment, determined the ratio of energy used to nitric acid obtained. As his aim was to isolate argon, he used a mixture of 1 vol. of nitrogen and 2 vols. of oxygen. From this mixture he obtained 49 grams of HNO_3 per kilowatt hour.[6] Rayleigh's work led Dougall and Howles[7] to a careful study of methods of increasing the yield. They employed an alternating current of 60 periods per second, with varied resistance. Their most important discovery was that, with a given potential, the ratio of acid formed to current employed falls as the current increases. Their best yield from the Rayleigh nitrogen-oxygen mixture was 65 grams of nitric acid, and from air 33.6 grams of nitric acid per kilowatt hour, with 0.15 ampere current, 60 periods per second and 8,000 volts potential, while with 0.3 ampere about half the relative amount of acid was obtained. Their work was confirmed and enlarged by DeKowalski and Moseicki,[8] who showed that the yield of acid can be increased by using a rapid alternating current. With a current of 0.05 ampere, 6,000 to 10,000 periods per second and a tension of 50,000 volts, they obtained 55 grams HNO_3 per kilowatt hour from air.

[1] Phil. Trans., 186, 197.
[2] *Ibid.*, 78, 473.
[3] P. Roy. Soc., 30, 174.
[4] German Patent, No. 88,320.
[5] Phil. Trans., 186, 197.
[6] In this report the weight of nitric acid—HNO_3—per kilowatt hour, calculated from the amount of nitrogen oxidized, is used as relative measurement. It must not be understood that concentrated nitric acid was actually made.
[7] Manchester Memoirs, 44, 1; Various patents.
[8] Société Internationale des Electriciens, 2 Serie, III., No. 26. Electrotechnische Zeit., 1904, p. 27.

Bradley and Lovejoy's[1] patent was exploited by the Atmospheric Products Co., with works at Niagara Falls. For the continuous arc of weak intensity used by Rayleigh, Dougall and de Kowalski, these two later inventors raised the yield of acid by substituting arcs quickly torn away from the electrodes, thus giving a rapid series of isolated sparks or arcs. Their apparatus is illustrated in Fig. I. A rotating vertical axis car-

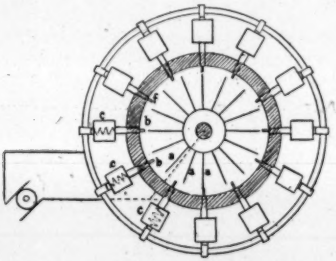


Fig. I.

ries a circle of electrodes *a*, projecting from the axis at a right angle to it. Opposite to them, on the periphery of a circle, are a number of electrodes *b*, each connected with induction coils *c*; as the axis rotates, a moving electrode approaches a fixed electrode and an arc forms, which tears off as the axis rotates, but, in the interval, other electrodes have approached, forming new arcs. The resistance of the induction coil causes a sudden expenditure of energy at the instant the arc is torn away, with resulting high temperature; as, in the next instant, no heat is generated at this point, sudden, extreme cooling occurs. Their maximum yield was 88 grams of nitric acid per kilowatt hour. They used direct current and 10,000 volts tension. Work stopped in the summer of 1904.

Before further consideration of the technical processes, let us turn to the theory of the oxidation, as stated by Dr. Brode. When air is heated to about 2000° or higher, nitrous gases are formed, no matter whether the high temperature is attained chemically, by burning hydrogen, magnesium, etc., or physically, using electric arcs and sparks, or higher resistance. Therefore, the conditions of oxidation are neither chemical nor electrical, but simply thermal. When the nitrous gases thus formed are shaken with water, a mixture of nitric and nitrous

[1] Electrochem. Ind., 1, 20, 100, 386. Cf. various patents.

acids is produced, $H_2O + 2NO_2 = HNO_2 + HNO_3$. That nitrogen peroxide, NO_2, was not formed in the flame is proved by the fact that this gas decomposes into nitric oxide and oxygen at 620°. Similarly, nitrous oxide, nitrogen tetroxide, nitrogen trioxide and nitrogen pentoxide are excluded. There remains, therefore, only nitric oxide, which is formed in the flame and, on cooling, combines with oxygen of the air to form nitrogen peroxide.

The equilibrium of the reaction $N_2 + O_2 \rightleftarrows 2NO$, according to the law of mass action, is governed, for every temperature, by the function $K = \frac{c_{NO}^2}{c_{O_2} c_{N_2}}$. As the equilibrium of a chemical reaction changes in the sense that the concentration of substances whose formation is endothermic increases with the temperature, and as the formation of nitric oxide is endothermic, K rises with increasing temperature and approaches zero as the temperature falls. If the reaction velocity remained the same for all temperatures, no matter how great the value of K at high temperatures might be, no nitric oxide would be formed, because, at a given high temperature, if a certain concentration were attained, as the temperature was lowered the concentration would lessen with the lowering. The reaction velocity, however, depends chiefly on temperature; in this reaction it is immeasurably small at 1000°, very great at 2000°. This change renders it possible to nearly retain the high temperature concentration by quickly cooling the gases; of course some nitric oxide must be decomposed as the temperature falls, but the more rapid the cooling the less the decomposition.

Hence the ideal nitric oxide formation requires high temperature and rapid cooling. These conditions may be realized in a laboratory by an electrically heated platinum wire in the axis of a cooled tube, but the temperature at which the yield of nitric oxide is enough for a technical process lies far above the fusion point of platinum, and, for technical use, only electric discharges need be considered. These are of two types, arcs and flames; before comparing them we must understand the nature of the flame.

Spottiswoode's observations were carried further by Rayleigh and by Kowalski, who showed that an electric flame cannot be formed directly by a constant tension current, but that high resistance, by induction coils, is needed. Muthmann and Hofer[1] published an extended study of the flame which is carried on by Brode in a part of this monograph. They tried to determine the scientific basis of the technical processes, and were the

[1] Ber. d. chem. Ges., 36, 438 (1903).

first to prove clearly that the nitrogen oxidation is a purely thermal effect. They showed that, in the electric flame, an equilibrium of nitrogen, oxygen and nitric oxide is formed. Their description of the flame is as follows: The nitrogen-oxygen flame resembles in form a gas flame issuing from a slit burner. Three zones can be distinguished; zone 1 is a greenish white band of light, filling an arched space between the electrodes; above this is zone 2, a luminous, greenish blue zone which, with 4 cm. distance between electrodes, is about 5 cm. high; this is surrounded by zone 3, a large outer zone "pale yellowish-brown" in color. The size of the flame increases with the distance between the electrodes. Muthmann thinks that electrical action occurs only in zone 1, the oxidation of nitrogen to nitric oxide in zone 2, and the oxidation of nitric oxide to nitrogen peroxide in zone 3. Brode proves that electrical action is confined to zone 1, by introducing solids into the three zones; a solid may be brought into zone 2 or 3 without altering the strength of the current or its tension, but if a solid is brought into the upper part of zone 1 it flattens the arch, shortening the distance of zone 1 between the electrodes, thus increasing the strength of the current and, if the solid is introduced into the lower part of zone 1, it lengthens the zone and thus decreases the current strength.

Enough has been said of the flame to understand a comparison of the technical value of flame and arc. In the flames the hottest space is comparatively small, and the different temperature zones are approximately equal in area, hence the conditions for cooling are bad. With intermittent sparks or arcs a larger heated area for nitric oxide formation is secured, while the cooling process is rapid, because there are no zones of diminishing temperature as in the flame, and also because, while a flame is a continuous source of heat, broken arcs or sparks give alternate heating and cooling periods.

To sum up: The technical process should employ intermittent arcs or sparks, should work with low current and high resistance, should use a rapid alternating current, should secure temperatures of 2000° and upwards, should provide rapid cooling of the gases, and should have a sparking chamber so arranged that a current of air passes quickly but thoroughly through to the zone of highest heat and out of the chamber. It will be noticed that the need of a low current must mean low total yield of acid, and this is the weak spot in the previous processes. Birkeland, who is professor of physics in the University of Christiana, and Eyde, who is a Norwegian civil engineer, have invented a process[1] which meets these demands

[1] Electrochem. Indus., 2, 399. Various patents.

excepting that for a low current ; the inventors, instead of working with arcs of the lowest possible amperage, make the first technical application of a phenomenon previously known to physicists, the action of the magnetic field on the arc. Both Witt and Brode think this process a technical and financial success ; Witt is, without doubt, an authority on questions of technical chemistry.

The inventors use a powerful current of electricity in the form of great glowing electric discs, which are built up of arcs deflected by powerful magnets as shown in Figs. II. and III.

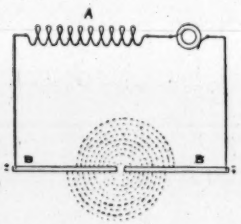


Fig. II.

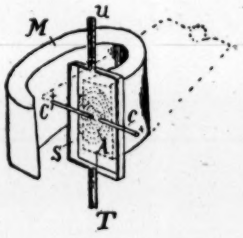


Fig. III.

An induction coil, Fig. II., A is introduced into the circuit and the electrodes BB are placed horizontally. Vertical to the electrodes are powerful electromagnets ; the arc formed between the electrodes is blown away, as it were, by the influence of the magnetic field, and at once a new arc is formed which is blown away ; this process can be repeated 1000 times a second, though in practice only a few hundred arcs per second are used. With alternating current arcs and direct current magnetic field, or *vice versa*, the arcs vibrate between the electrodes as circular discs, as indicated in Fig. II. With 30 kilowatts energy discs of 1 meter diameter can be formed. The electrodes are brought so close together that they would be short-circuited were it not for the magnetic field whose dispersing influence gives sufficient resistance. The hollow electrodes are of copper, cooled internally by water. Fig. III. illustrates the application. M is a magnet ; between its poles is the discharge furnace A, resembling in form a shallow covered box, into which extend the electrodes C C' ; the electric disc is indicated by the circular dotted lines ; air passes rapidly

through the tubes T and *u*, over the disc and out of the furnace. In practice the furnace is built of fire-clay plates, covered externally with copper, and is shown in its latest form in Fig. IV., where A A are electrodes, B B magnets.

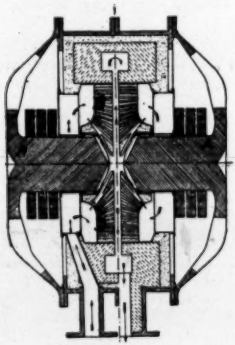


Fig. IV.

This large furnace works with an energy of 500 kilowatts and 5000 volts tension, with alternating current arcs and direct current magnetic field. The electric disc is *2 meters* in diameter, and its dazzling, sun-like appearance is photographed in Fig. V.

The yield is about 100 grams of HNO_3 per kilowatt hour, an advance on the 88 grams of the Bradley and Lovejoy process, but this comparison in no sense represents the immense advantage of the Birkeland-Eyde process. The point is that, with the electric disc, the inventors employ 500 kilowatts energy in one furnace, whereas, by other processes, not more than 500 watts could be employed in one furnace. Thus Birkeland and Eyde can make 1000 times as much acid in one furnace in a given time as any of their predecessors. Their new factory at Notodden is equipped with three of the large furnaces described, and the yield is the amount of nitrate corresponding to 1500 kilos of HNO_3 per 10-hour day. The company exploiting the patent has options on the use of Norwegian waterfalls which will yield 350,000 horse power at a very low price, with water carriage to the sea.

Fig. V.

The product of the process is a mixture of unchanged air and nitric oxide, containing 2 per cent of the latter, the oxide, of course, combining with the oxygen of the air to form dioxide, which, in turn, with water yields nitric acid and nitric oxide, $3NO_2 + H_2O = 2HNO_3 + NO$. This diluted product is unavoidable, as shown by Naville and Guye, but forms the chief objection raised by critics against all previous processes. The following figures will show the reason: The actual cost of the electrical energy required for the oxidation is small. If we say 0.5 pfennig per kilowatt hour (at Notodden it is less) and assume that 10 kilowatt hours energy = 1 kilo HNO_3; or, in other words, that the energy required to produce the nitrous gases sufficient to yield 1 kilo of concentrated nitric acid costs 5.2 pfennigs or about 1.2 cents, then, as the German market price of crude nitric acid is 50 pfennigs or 12 cents per kilo, this is 10 times the price of the energy; hence, as Haber pointed out in 1903,[1] the difficulty is less in the production of the nitrous gases than in changing these gases to concentrated nitric acid. This last problem has not yet found its technical solution; doubtless it will be solved, just as the similar problems of the technical treatment of sulphur dioxide to form sulphuric acid and sulphur trioxide have been solved. For the present, the only economical treatment is to market the product in the form of calcium nitrate. In former processes the nitrous gases were conducted directly into milk of lime, forming a mixture of nitrate and nitrite, which, though a good fertilizer, was very hygroscopic and impossible to handle commercially.

The methods by which Birkeland and Eyde have improved and simplified this treatment are interesting: The hot nitrous gases coming from the furnace are cooled by passing under boilers, thus generating steam which is used to concentrate the calcium nitrate solutions. The cooled nitrous gases reach the "oxidation towers," which are lined with acid-proof stone, and merely serve to lessen the movement of the gas current, giving the gas more time for oxidation. The gases now go to the "absorption towers;" these are built of granite and filled with pieces of quartz. Water drips constantly through this tower, absorbing the dioxide; the nitric acid which flows out is returned again and again until it is concentrated to 50 per cent HNO_3. The gases from the three Notodden furnaces pass through 8 absorption towers, which extract the acid so far that further treatment with water is useless. The gases then pass through two towers filled with milk of lime and one filled with

[1] Z. Elek. Chem., 9, 385.

dry quicklime; all oxidized nitrogen is absorbed; the product is chiefly calcium nitrite, which is treated in closed vessels with some of the 50 per cent nitric acid, and the resulting nitrous gas passed into the "oxidation towers," where it is oxidized quantitatively to nitric acid. All of the nitric acid is neutralized with limestone, the solution is added to that from the nitrite treatment, evaporated and fused; the molten mass is run into iron drums and solidifies on cooling.

This product is not the hygroscopic nitrate $Ca(NO_3)_2$, but a basic nitrate which powders readily and, in contact with the soil, *i. e.*, carbon dioxide and moisture, breaks down into normal calcium nitrate and calcium carbonate; that this is good for soils poor in lime, that lime is a better base for fertilizer than the sodium of Chili saltpetre, and that the synthetic nitrate is free from the harmful perchlorate and chlorides of Chili saltpetre, are obvious facts. Indeed, the demand for the synthetic nitrate exceeds the supply.

The Chilean statistician, Vergas,[1] basing calculations on the exportations of Chili saltpetre since 1840, proves that the next 20 years will completely exhaust the South American deposits. No other large deposits are known, nor is their discovery probable.

In the future we must obtain the nitrogen compounds required for agriculture, explosives and all other scientific and technical purposes from the nitrogen of the air.

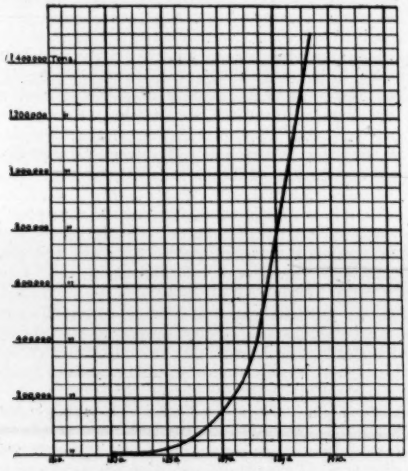
Fig. VI. shows the curve indicating the export of Chili saltpetre from 1830 to 1905. It will be seen that in 1905 1,500,000 tons were exported. Of this $\frac{1}{5}$ was utilized for making nitric acid and other nitrates, the other $\frac{4}{5}$, or 1,200,000 tons, were put on the soil as fertilizer.

Four-fifths of the products from atmospheric nitrogen, then, will be needed for the soil. Thus far there are four methods of combining this nitrogen, one bacterial and three chemical. The bacterial absorption of nitrogen is, at present, confined to leguminous plants, and unless a more active breed of bacteria can be developed, bacterial action, while valuable, cannot replace the use of Chili saltpetre.

The formation and decomposition of nitrides is the second method. This works best with lithium, but barium or calcium might be substituted: $6Li + N_2 = 2NLi_3$ and $2NLi_3 + 6H_2O = 6LiOH + 2NH_3$. Now it can be shown that the electric energy required to regenerate this quantity of metallic lithium from the hydroxide, by electrolysis, is about half of that required to oxidize the equivalent quantity of nitrogen to nitrous

[1] Chem. Indus., 1904, p. 29.

gases, while the ammonia generated could be absorbed by water or acid at small expense; yet technical difficulties and the certain loss of some of the valuable metal in the electrolysis



Weltverbrauch an Chilesalpeter 1830—1905.

Fig. VI.

forbid any practical application of this principle, for the present at least.

The third method is Franks' well known process, in which pure nitrogen, not air, is absorbed by heated calcium carbide, forming calcium cyanamide, which is a valuable fertilizer. This process is on trial technically. Whether the calcium cyanamide can compete with the synthetic nitrate is doubtful.

The fourth method is the nitrogen oxidation.

Of one thing we may be certain, by the time the Chili saltpetre beds are exhausted, chemists and engineers will be ready with practical and economical methods of utilizing atmospheric nitrogen to meet the demands of agriculture and industry.

E. Renouf.

Esterification.

The experiments of E. Fischer and A. Speier,[1] proving that mixtures of organic acids and absolute alcohol could be readily esterified by the use of small quantities, not exceeding 1–5 per cent, of hydrochloric or sulphuric acid, are justly regarded as a most important advance in the preparation of this class of compounds. Later, the present writer[2] showed that ordinary 90–95 per cent alcohol could be employed with equally good results, provided that the quantity of mineral acid was increased. No improvement has been made in the application of this reaction since that time until the recent publication of a paper by A. Bogojawlensky and J. Narbutt,[3] recording the results of an investigation of the action on mixtures of various organic acids and alcohol, of the following dehydrated sulphates: Sodium, ferrous iron, nickel, manganese, copper, cobalt, zinc and potassium pyrosulphate. Sodium sulphate was devoid of action, as was to be expected from the ease with which it parts with its water of crystallization. As a rule, the best results were obtained with potassium pyrosulphate and copper sulphate, with which, therefore, the majority of the experiments were conducted. The former is equally well applicable to aliphatic and aromatic acids, the latter chiefly to the aliphatic acids, but mixtures of copper sulphate (35 grams), with concentrated sulphuric acid (1 gram), gave good results with aromatic acids. In many cases the yields were better than by Fischer's method and the isolation of the ester is usually effected by simply decanting from the salt and fractionating directly. Two other points of considerable interest are brought out in the paper. The one concerns the very marked influence on the yield of ester exercised by traces of sulphur trioxide, such as are present in dehydrated sulphates; for instance, succinic acid (20 grams), alcohol (80 grams) and ferrous sulphate (25 grams), after boiling during 4 hours, gave 85 per cent of the theoretical yield of neutral ester, but on repeating the experiment with anhydrous ferrous sulphate, which had been freed from sulphur trioxide by repeated extraction with alcohol, the yield was only 34 per cent of the theory. An experiment was carried out with malonic acid, alcohol and the zeolite chabasite, which readily absorbs moisture, in order to ascertain if the acceleration in the esterification, which is caused by strong acids and by certain salts, is due simply to the absorption of the water formed by the union

[1] Ber. d. chem. Ges., **28**, 3252 (1895).
[2] This Journal, **21**, 256 (1899).
[3] Ber. d. chem. Ges., **38**, 3344 (1905).

of the organic acid and alcohol, or whether these accelerators have some other influence. The result showed that the zeolite had no appreciable effect on the production of ester.

It is to be hoped that the authors will continue their work, because it promises to be of considerable importance for the preparation of esters and may, possibly, help in the elucidation of the mechanism of this puzzling reaction.

Shortly after the publication of the preceding paper J. Wade[1] described a method for the continuous preparation of esters at 100°, in the presence of sulphuric acid. Markownikoff[2] described a continuous method of esterification 30 years ago, but stated that the reaction does not take place below 130°. Wade finds that the chief factor for success is the rate and extent of the heating; if the flask containing the mixture is placed *on* a water-bath the reaction soon ceases, but if it is *immersed in* the bath, so as to volatilize the water produced by the reaction, the process is truly continuous. It may be interrupted at any time without detriment, and there is no delay in restarting when once the materials have regained the necessary temperature. The presence of sulphuric or some other strong acid is essential, but a large quantity of it is a disadvantage; charring is unusual, so that it is seldom that sulphuric acid cannot be employed. The author states the conditions for the production of ethyl acetate as follows: Three volumes of alcohol are mixed with 2 volumes of acetic acid, and 2 volumes of this mixture are added to 1 volume of sulphuric acid in an Erlenmeyer flask, which is immersed in a water-bath until distillation commences; this may require as much as 30 minutes, but depends on the ester. The mixture of alcohol and acetic acid is then added through a funnel with a fine stem, as in the ordinary preparation of ether. The process is fairly economical, because most of the excess of alcohol is recovered in the purification of the product.

Details of the preparation of other esters are reserved for a subsequent communication, which will be awaited with considerable interest. The method is applicable to all the simple aliphatic and to many of the more complex and aromatic esters, the operation being carried on under reduced pressure when working with the less volatile ones. J. Bishop Tingle.

[1] J. Chem. Soc., 87, 1656 (1905).
[2] Ber. d. chem. Ges., 6, 1177 (1873).

REVIEWS.

SECOND YEAR CHEMISTRY. A Handbook for Laboratory and Class Work. By EDWARD HART, PH.D., Professor of Chemistry in Lafayette College. Easton, Pa.: The Chemical Publishing Co. 1905. Price, $1.25.

Professor Hart's preface explains the difference between his book and most laboratory manuals as follows: "In teaching qualitative analysis I have often thought that if the beginner first made some careful quantitative determinations, he would quickly learn the necessity of extreme care and that all his subsequent work would be thereby improved."

In the first 56 pages the author treats, with suitable experiments, of molecules and atoms, properties of gases, gas analysis, dissociation, dissociation in solutions, the chemical balance, volumetric analysis and gravimetric analysis. Seventy-five pages are given to qualitative analysis, and 22 pages, at the close, to different quantitative determinations.

On the whole, the little manual makes a very favorable impression, and we can well believe that Professor Hart has obtained good results with this method. E. R.

ENGINEERING CHEMISTRY. A Manual of Quantitative Chemical Analysis for the Use of Students, Chemists and Engineers. By THOMAS B. STILLMAN, M.Sc., PH.D., Professor of Analytical Chemistry in the Stevens Institute of Technology. Third edition, with 139 Illustrations. Easton, Pa.: The Chemical Publishing Co. 1905. Price, $4.50.

In a review of the second edition of this book,[1] Professor Mallet refers to the absence of chapters on lime, lime mortar, stucco and explosives. It is to be regretted that these chapters are also lacking in this third edition. However, the book contains many improved methods of analysis and other important additions, especially the chapters on lubricating oils, cements and asphalt. The volume is well indexed and is provided with abundant references. In its present form this is one of the best practical manuals for engineers and students of engineering. E. R.

THE ELECTROLYTIC DISSOCIATION THEORY, WITH SOME OF ITS APPLICATIONS. An Elementary Treatise for the Use of Students of Chemistry. By HENRY P. TALBOT, PH.D., Professor of Inorganic and Analytical Chemistry, and ARTHUR A. BLANCHARD, PH.D., Instructor in Inorganic Chemistry at the Massachusetts Institute of Technology. New York: The Macmillan Co. London: Macmillan & Co., Limited. pp. 84. Price, $1.25.

The appearance of this admirable little volume will be wel-

[1] THIS JOURNAL, 25, 517.

comed by all who are interested in the teaching of chemistry from the standpoint of the generalizations reached by physical chemistry. It is indicative of the signs of the times that books of this character are demanded by teachers and students. The general impression is gaining ground, and gaining it rapidly, that the fundamental generalizations which have done so much towards placing chemistry upon a scientific basis, should be taught in the early stages of the study of this subject. They should, of course, be introduced cautiously and in a very elementary form. The chemistry of the atom should not be taught for a year or two and then the student be told that this was all wrong, that atoms do not, in general, react chemically, but that what actually reacts are the ions.

If the student is started in this fashion the question is, how long will it require for him to recover from these first erroneous impressions, or will he ever completely recover? In many cases it is doubtful. If we ask, why continue along the old lines, about the only answer is that the atom is simpler to teach than the ion. This, even if true, would be a sorry reason for teaching what, later, must all be unlearned.

It seems a fair question to ask whether the real reason, in many cases, why the chemistry of the atom is taught, is not to be found in the fact that this is the chemistry which the teacher learned in his earlier days, and it is easier to continue in the old beaten tracks than to become familiar with the newer developments?

The volume under review will contribute its share towards changing this condition of things. The contents are judiciously selected, and the book is clearly written. Chapter I. deals with evidences for the theory of electrolytic dissociation; Chapter II. with the law of mass action and the chemical behavior of electrolytes; Chapter III. with electrolytic solution pressure; Chapter IV. with oxidation and reduction; and Chapter V. with the more common ions and their characteristics. This chapter is especially valuable in connection with the operations of qualitative analysis.

The book is heartily recommended to students, and especially to teachers of elementary chemistry. H. C. J.

AN ELEMENTARY LABORATORY COURSE IN CHEMISTRY. By FRANK B. KENRICK, M.A., PH.D., Lecturer in Chemistry, University of Toronto, and RALPH E. DELURY, M.A., Fellow in Chemistry, University of Toronto. Toronto: Morang & Co. 1905. Price, $1.00.

In reviewing this volume it must be kept in mind that it is a manual of laboratory work to accompany a course of lectures for beginners in inorganic chemistry, and that the exceptional

features of the book are intended, as we shall see, to meet exceptional conditions.

The preface says: "Owing to the shortness of time in the laboratory, many important principles have been necessarily omitted. The principles especially emphasized, however, are those which, on account of their inherent difficulty or of some traditional error in previous instruction, generally appear to give most trouble to the student."

The experiments—many of them roughly quantitative—are chosen with excellent skill for the purpose in view, which is to devote all the time to illustrating the chief laws and principles of chemical action, thus omitting the systematic laboratory study of the properties of the elements and their compounds, which forms a part of the first year laboratory work in most American colleges. The subjects, which are very clearly treated and accompanied by good, and often ingenious experiments, include solution, crystallization, combustion, combining weights, acids, bases, salts, gravimetric and volumetric analysis, volume relation of gases, reversible reactions, mass law, electrolytic dissociation.

When the time available for laboratory work is very limited, it is, perhaps, better to employ it as is done in this book than to attempt to cover as much ground as is common in the average beginners' laboratory course. Should it be necessary to choose, it is better to understand combustion than to know the properties of all of the oxides of nitrogen. If we regard this book as a protest against the too common method of cramming the beginner with details, while making little attempt to study experimentally the fundamental laws of chemistry, it merits respectful attention.

One peculiarity challenges notice. The authors say in their preface: "All reference to the atomic and molecular theories have been avoided, not because the authors are prejudiced against these excellent hypotheses, but in order to counteract a prejudice in the opposite direction on the part of the students. A large number of students still continue to come to the university with their minds simply stuffed with atoms and molecules, which they take to be the fundamental facts of chemistry."

This experience is not new, probably all college teachers have to combat such fallacies, often brought about by injudicious instruction in the preparatory school; it is true that teachers generally do not apply such drastic discipline as to forbid further indulgence in atoms and molecules, but this may be necessary in Ontario.

Let us examine the authors' plan; instead of atoms they use the idea of combining weights, which they call "reacting weights." Of course it is possible to study most elementary principles and facts of chemistry without reference to atoms and molecules; the question is, does it pay? Does the student get clearer ideas without them? If a lion should hold the path, like ozone for instance, one can pass by on the other side and silently ignore it, but some things cannot be ignored and these are discussed in an appendix; for example, the question arises, why write hydrochloric acid HCl and not H_2Cl_2 or H_3Cl_3? here is the explanation:

"It has been discovered that the weights of equal volumes of gaseous chemical substances stand, approximately, in the ratio of simple multiples of their reacting weights when the pressure and temperature are the same. Hence, by choosing these particular multiples of the reacting weights, the numbers obtained will represent, approximately, the weights of equal volumes of the gaseous substances. These are called molecular or formula weights because the chemical formulæ are so chosen as to represent these weights, in addition to the composition."

Is this an improvement on the explanations given commonly? Is the molecular weight less hurtful to the student when christened formula weight?

Some students come to universities overstuffed not only with atoms and molecules but with ions and electrons, and even with reacting weights. Are we, therefore, to throw all these conceptions overboard? However, we must remember that this is only a laboratory manual and that in the lectures the authors probably explain to the student the proper value of those "excellent hypotheses," the atomic and molecular theories.

E. R.

MONOGRAPHIEN ÜBER ANGEWANDTE ELEKTROCHEMIE. XX Band. Elektrolyse geschmolzener Salze. Erster Teil. Verbindungen und Elemente. von RICHARD LORENZ, PH.D., O. Professor für Elektrochemie und physikalische Chemie, am Eidg. Polytechnikum in Zürich. Mit 9 in dem Text gedruckten Abbildungen. Halle a. S.: Druck und Verlag von Wilhelm Knapp. 1905. pp. 217. Price, M. 8.

The author's name on the title-page of this volume leads us to examine it with high expectation, because Lorenz is an authority in the field. We are not disappointed; we find the whole story of the electrolysis of fused salts, from the qualitative preparative point of view, told with great clearness and sense of proportion. Nothing is omitted, all published work is referred to, the lists of patents are complete and yet it is interesting reading; indeed, while we generally look on a mono-

graph like this as a reference work, we find that many of the chapters, notably those on the electrolysis of sodium chloride and sodium hydroxide, of cryolite and of the chlorides of the rare-earth metals, are of absorbing interest.

The author will devote a second volume to the application of Faraday's law, to conductivity and to the subject of electromotive power. E. R.

DIE ELEKTROCHEMIE DER ORGANISCHEN VERBINDUNGEN. Von DR. WALTHER LÖB. Dritte erweiterte und umgearbeitete Auflage von: Unsere Kenntnisse in der Elektrolyse und Electrosynthese organischer Verbindungen. Halle a. S.: Wilhelm Knapp. 1905. Price, M. 9.

The book is a summary of the work that has been done along the line of the application of the electric current to organic substances. All the principal classes of compounds have been subjected to experiment and the number of reactions that may be effected by the electric current is surprisingly large. The nitro compounds have yielded, perhaps, the most varied and valuable series of products resulting from electrolytic action.

Not only has the direct current been used with great success in producing chemical reactions, but also the alternating current and, in fact, almost all forms of electrical energy. Two factors which must be reckoned with in all operations are the selection of electrodes and the current density. Condensing agents are often used to cause the reaction to stop at a definite stage.

The theoretical side of electrochemical phenomena is treated at some length in the book. The manner in which organic compounds dissociate when treated with the electric current is discussed, and its theoretical bearing clearly stated. The processes which take place around kathode and anode are fully described.

Reactions are classed as primary when the end products have been formed by phenomena directly traceable to the action of the current, and as secondary when the products are the result of a rearrangement or condensation.

The technical value of the electric current in the manufacture of organic compounds is shown to be very great and, since this is only a new field, it is difficult to predict to what extent its application will be carried.

Constant reference is made to the investigations of Löb, Elbs, Walker, Haber, Müller and many others, who are active in the development of this new chapter of organic chemistry.

The book may be recommended to all who are interested in the extension of this important field of research. C. W. G.

JAHRBUCH DER CHEMIE. Bericht über die wichtigsten Fortschritte der reinen und angewandten Chemie. Unter Mitwirkung von H. BECKURTS, C. A. BISCHOFF, ALFRED COHN, M. DELBRÜCK, J. M. EDER, TH. FISCHER, P. FRIEDLAENDER, C. HAEUSSERMANN, A. HERZFELD, W. KÜSTER, J. LEWKOWITSCH, A. MORGEN, F. QUINCKE, A. WERNER. Herausgegeben von RICHARD MEYER. XIV. Jahrgang, 1904. Braunschweig: Vieweg und Sohn. 1905. Price, M. 14.

The Jahrbuch for 1904 appears after a considerable delay, which the publishers promise to avoid in the future, as they have in the past.

It is a complete review of the progress of the year, arranged so that each piece of work may be considered in relation to other work on similar topics.

The work, as a whole, is well done, as we should expect from the list of co-workers. There are some curious omissions. Several important physical chemical articles, published in this JOURNAL, are omitted and, by a singular coincidence, important work by the same authors, published in the *Zeitschrift für Physikalische Chemie* is also either omitted or barely mentioned, although the other articles in the *Zeitschrift* are reviewed. E. R.

THE POLARISCOPE IN THE CHEMICAL LABORATORY. An Introduction to Polarimetry and Related Methods. By GEORGE WILLIAM ROLFE, A.M., Instructor in Sugar Analysis in the Massachusetts Institute of Technology. New York and London: The Macmillan Company. 1905. pp. 320.

The subject of polarimetry has, for some time, been of practical importance on account of its use for the commercial testing of sugars. It has recently acquired a scientific significance in connection with the dynamics of the reaction of the inversion of cane sugar. We are frequently in need of information in reference to the use of the various polariscopes, and the significance of the results obtained. The present volume supplies just this information.

The several sections deal principally with the polariscope, the saccharimeter, polarization of cane sugar, commercial methods, determination of sucrose in the presence of other optically active substances, sugar-house and refinery methods, chemical methods of determining sugars, starch and starch products, applications of the polariscope in scientific research, application to chemical analysis.

It will be seen from the above that this review refers to a book which is of both scientific and technical value. It is to be hoped that it will meet with the wide reception that it deserves. H. C. J.

EXERCISES IN QUANTITATIVE CHEMISTRY. By HARMON NORTHOP MORSE, Professor of Analytical Chemistry in the Johns Hopkins University. Boston, New York, Chicago, London: Ginn & Co. 1905. pp. xx + 556. Price, $2.00.

Those shelves of our chemical libraries which are devoted to books on quantitative analysis have, if we have been sympathetic purchasers, filled somewhat over-rapidly of late. Many of the contributions to this branch of chemical literature have been the product of careful thought and a painstaking selection of reliable methods, but they have, almost without exception, followed a conventional treatment of the subject. It is, therefore, a real, as it is an unusual pleasure to receive a volume which presents a course of instruction in quantitative chemistry with distinctive features, and one which is the product of the long experience of a successful teacher.

Professor Morse points out that, with the increasing demands made upon the time of the student of chemical science for instruction in other branches of chemistry, the selection of a suitable general course of instruction in quantitative practice has become increasingly perplexing. He has, therefore, formulated his course in such a way as to give familiarity with the greatest practicable variety of methods and operations, and has included not alone methods of chemical analysis, but also those involving accurate determinations of specific gravity, and determinations of molecular weights. An incidental, but striking and valuable feature of the course, is the thoroughness of the practice which it affords in the determination of the limitations and the accuracy of the instruments employed, a point upon which much stress is laid. The course is, then, one in quantitative chemistry, not analytical chemistry.

The first four chapters deal successively with the balance, the barometer and thermometer, the calibration of eudiometers and the measurement of gases, and the calibration and graduation of apparatus for the measurement of liquids. The first chapter is noticeable for its thorough discussion of methods of testing balances and weights.

Chapter V. deals with standard solutions, Chapter VI. with the determination of specific gravity, Chapter VII. with molecular weights, and Chapter VIII. with the purification of substances, including the general operations of filtration, washing of precipitates, and the like. Chapters IX. to XXII. (pp. 209–516) include quantitative procedures of the most varied character, and the combination of volumetric with gravimetric methods, as well as the application of one or both to organic compounds is unusual and worthy of attention. There are among the exercises examples of the processes involved in gas

analysis, food analysis, and electrolysis, with a clear and concise statement regarding electrical units and the apparatus employed in this class of work. In the last two chapters certain new and useful electrical heating appliances are described, together with an electrical method for the combustion of organic compounds.

The procedures are given in considerable detail and the book contains a great deal of valuable information which cannot be indicated in a brief summary, it is all presented in easily readable form. The particular analytical procedures which the author has selected will, doubtless, sometimes excite comment. It would, for example, seem natural to give preference to the Drown method for the determination of silicon in irons or steels, especially since the dehydration of silicic acid by sulphuric acid is not otherwise emphasized, or to replace copper ammonium chloride by copper potassium chloride in the determination of carbon in irons, in view of the acknowledged sources of error sometimes involved in the use of the former reagent. The omission of a procedure for the separation of iron from manganese is also noticeable, particularly the omission of a process so distinctive in its character as the basic acetate method. The use of the atomic weights based on hydrogen as unity, the retaining of the older definitions for the molecular changes of boiling or freezing point, and an apparent preference, in many instances, for the methods given in the manual of Fresenius may possibly raise a question in the mind of the reader whether or not the author is just a bit too much inclined to adhere to older methods, or points of view, rather than to incorporate more recent work. But these, so far as the main purpose of the book is concerned, are minor matters and should not deter any teacher or student from according it the careful examination which it undoubtedly deserves.

The book is thoroughly indexed and exceptionally well printed and bound. H. P. TALBOT.

BEET SUGAR MANUFACTURE AND REFINING. Vol. I.: Extraction and Epuration. By LEWIS S. WARE. New York: John Wiley & Sons. London: Chapman & Hall. 1905. Price, $4.00.

This volume of 537 pages of text, yet treating of only two of the basic processes of beet sugar manufacture, is by far the most comprehensive work on beet sugar technology which has appeared in the English language.

The author states that he limits his work strictly to a compilation of the data and discussions of European literature as best giving expression to the practice of the world's leading experts. He refrains from consideration of American methods on the ground that he would be obliged to criticize "some very

glaring blunders." No doubt many blunders have been made in America, yet it would seem that processes of beet sugar manufacture are not yet so far developed as to be standard even in Europe. The author says, in his preface: "In fact, throughout the entire realm of sugar manufacturing, there is a vast budget of contradictions." Hence a discussion of methods extant in successful American factories might have been of profit, particularly as it is a matter of common knowledge that foreign experts, as a rule, have not been satisfactory in American practice.

The 22 pages of the introductory chapter discuss the economics of the industry from a practical standpoint. The suggestions for utilizing beet sugar factories during the "dead" season are most interesting. Incidentally, the reviewer dissents from the author's carbonation scheme for manufacturing *milk* sugar as quite impracticable, although it might be that the plant could be utilized in other ways for this purpose.

Considering the book as a whole, the material is judiciously chosen, and evidently by an expert of some experience. The references to authorities are very complete and the illustrations are many and excellent. In the opinion of the reviewer, however, the book is somewhat marred by the style of the English, which occasionally follows the German and French constructions so literally as to make it evident which was the language of the original, and, in fact, almost to permit of reproduction of the foreign text. Naturally, in such cases, the English is clumsy and lacks compactness, particularly in excerpts from the German. Such expressions as "conservation of beets," "surveillance of washer" (machine), "fixation of knives" (in slicing machines) possibly may have a certain vogue in beet sugar factories here, but certainly are not those of the best usage; and "arrival and departure of the juice into the diffusers," "forged iron piping" and "axis of rotation" (for shafting) are some of the examples, among others, which might be cited as especially unhappy rendering into technical English. As a rule, however, the descriptive matter is clear enough to be readily understood by the engineer and manufacturer, who will be greatly assisted by the illustrations with which the book abounds.

The discussions of rationale of process are a valuable feature, and cannot fail to be instructive.

The book would have been improved if dimensions of machinery and other factory measurements had been expressed in the standards in common use in English-speaking countries.

The presswork, as a whole, is of high quality.

GEO. W. ROLFE.